

TABLE I. ^1H and ^{13}C Contact Shift Data for Nickel(II) and Cobalt(II) Hexakis Pyridine-N-oxide Complexes.^a

	Ni	Co
C_α	-2.58(0.06)	-3.57(0.20)
C_β	1	1
C_γ	-1.40(0.12)	-1.76(0.10)
H_α		-1.20(0.10)
H_β		1
H_γ		-1.60(0.10)
R_α	-15.0(0.3)	-19.5(1.6)
R_β	-7.0(0.2)	-6.5(0.5)
R_γ	-6.1(0.5)	-7.2(0.3)

^a Normalized for the β values (standard deviations in brackets). Isotropic shifts for the β positions equal to 1 ppm correspond to the following molar fractions of bound ligand: 1.55 (^{13}C , Ni); 1.35 (^{13}C , Co); 8.3 (^1H , Co d_3 -acetonitrile); 10.7 (^1H , Ni d_3 -acetonitrile). R gives the ratio between ^{13}C and ^1H isotropic shifts at the same position.

for the CH_3 group attached to several aromatic heterocyclic ligands.⁹

Any attempt of interpretation of the observed ^{13}C and ^1H shift patterns cannot only rely on the idea that the spin delocalization mechanism occurs through the non-orthogonality between σ metal orbitals (in the idealized O_h symmetry) and π orbitals of the ligand.^{4,10} Presumably more than one spin delocalization mechanism are operative despite the strict similarity of the ^1H contact shift patterns for the two metal complexes. This apparent contradiction could be accounted for by assuming that only one spin delocalization mechanism gives rise to detectable shifts of the hydrogen nuclei.

Actually Drago *et al.*⁴ have suggested that proton contact shifts in $\gamma\text{-CH}_3\text{-py-NO}$ complexes are determined only by π spin delocalization. The σ contribution due to the highest energy filled σ molecular orbital is negligible because of the small proton coefficients in that MO. However, if also a σ spin density delocalization mechanism is operative (and it is sizeable on C atoms), different shift ratios between ^{13}C and ^1H shifts are expected. Of course this is just a possible path, not necessarily actual, to overcome the seemingly contradictory data. A further analysis, however, would be meaningful only if adequate theoretical tools¹¹⁻¹³ were available which allowed to compare the experimental results with sophisticated models including spin polarization mechanisms as well as the metal orbitals.

The comparison of the patterns of the ratios, R, between ^{13}C and ^1H shifts of each CH group for the two metal complexes is quite meaningful in understanding the role of the metal ion in determining the overall

spin distribution (Table I). From these data it appears that the difference in spin delocalization mechanisms due to the change of the metal ion is relatively small.

The shape of the nmr spectra deserves a further comment. The ^{13}C line broadening pattern qualitatively follows the contact shift pattern² ($C_\alpha > C_\gamma > C_\beta$) whereas T_1 values are smaller for C_α than C_β and C_γ . For example the T_1 values for a solution $1.1 \times 10^{-2} M$ of the cobalt complex and $2.9 M$ of the free ligand are 1.75, 4.75, 5.05 s for *ortho*, *meta* and *para* carbon atoms respectively. Presumably the carbon T_1 values are also affected by a dipolar coupling mechanism with the metal ion.¹⁴ On the contrary the pattern of the proton line broadening is not determined by the magnitude of the contact shifts but from the proton to metal distances. In every case the line width is larger for the nickel than for the cobalt complex, as expected.¹⁵

Acknowledgment

Thanks are due to Professor L. Sacconi for encouragement and helpful discussions.

References

- D. Doddrell and J.D. Roberts, *J. Am. Chem. Soc.*, **92**, 6839 (1970).
- I. Morishima, T. Yonezawa and K. Goto, *J. Am. Chem. Soc.*, **92**, 6651 (1970).
- "NMR of Paramagnetic Molecules", edited by G. La Mar, W. DeW. Horrocks and R. H. Holm, Academic Press, London, 1973.
- W.D. Perry, R.S. Drago, D.W. Herlocker, G.K. Poggenkopf and K. Kzworniak, *Inorg. Chem.*, **10**, 1987 (1971).
- I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chim. Acta*, **6**, 185 (1972).
- J.V. Quagliano, J. Fujita, G. Franz, D.J. Phillips, J.A. Wolmsley and S.Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1968).
- M.L. Wicholas and R.S. Drago, *J. Chem. Phys.*, **91**, 5963 (1969).
- M. Karplus and G.K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
- R.Z. Sagdeev and N. Molin, *Chem. Phys. Letters*, **5**, 47 (1970).
- R.W. Kluijber and W.DeW. Horrocks, *Inorg. Chem.*, **6**, 430 (1967).
- R.J. Fitzgerald and R.S. Drago, *J. Am. Chem. Soc.*, **90**, 2523 (1968).
- W.DeW. Horrocks, Jr. and D.L. Johnston, *Inorg. Chem.*, **10**, 1835 (1970); W.DeW. Horrocks, *ibid.*, **12**, 1211 (1973).
- M.J. Scarlett, A.T. Casey and R.A. Craig, *Aust. J. Chem.*, **23**, 1333 (1970); *ibid.*, **24**, 31 (1971).
- I. Solomon, *Phys. Rev.*, **99**, 559 (1955).
- N. Bloembergen and L.O. Morgan, *J. Chem. Phys.*, **34**, 842 (1960).

Bimetallic μ -Oxoalkoxides. X. A New Class of Polynuclear Complexes

T. OUHADI*, J. P. BIOUL, C. STEVENS, R. WARIN, L. HOCKS and PH. TEYSSIE**

Laboratoire de Catalyse Organique et de Chimie Macromoléculaire, Université de Liège, Institut de Chimie, Sart-Tilman, B-4000 Liège, Belgium

Received March 22, 1976

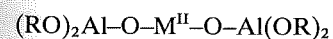
Cryoscopic data, as well as electronic, NMR and mass spectra are presented for a variety of bimetallic μ -oxoalkoxides; they indicate that, like simple metal alkoxides, these compounds are associated in organic solution. The importance of these intermolecular associations is related to the nature of the metals, but also to the structure of the alkoxy groups.

Introduction

Mixed metal oxides, specially those of transition metals, are well known for their interesting properties which have led to key applications in such fields as solid state physics and heterogeneous catalysis. In this frame, it was obviously tempting to undertake the tentative synthesis of molecules including $-\text{M}_1-\text{O}-\text{M}_2-$ units, soluble in organic media, but which would still mimic at least some of the important properties of the usual inorganic mixed oxides. These substances, enjoying combined properties due to the presence of different metals, could be of great interest in modelling the synergistic effects existing between oxo-bridged metals: such interactions usually result in extremely interesting electronic delocalizations and magnetic exchanges¹.

On the other hand, they could also represent good models of biologically important molecules, *i.e.* polynuclear complexes involving M_T-O bonds in molecular oxygen binding and activation.

In these prospects, we have accordingly prepared a series of compounds corresponding to the general formula



where M is Cr^{II} , Mn^{II} , Fe^{II} , Co^{II} , Zn^{II} , Mo^{II} and R an alkyl group (most often propyl or butyl).

These compounds, called μ -oxoalkoxides, were synthesized by two different methods. The first one involves a thermal condensation reaction between aluminum trialkoxide and a metal(II) acetate^{2a}, while the

* Present address: Abadan Institute of Technology, Abadan, Iran.

** Author to whom correspondence should be addressed.

second one is based on a carefully controlled hydrolysis of Meerwein's 2:1 double alkoxide complexes^{2b}.

It has already been shown that some of these μ -oxoalkoxides are excellent catalysts for the ring-opening polymerization of heterocyclic compounds such as oxiranes, thiiranes and lactones³. Moreover, the $\text{Fe}(\text{II})$ and $\text{Mo}(\text{II})$ derivatives are found to bind very rapidly molecular oxygen⁴.

The kinetics of these processes depend very strongly on the nature of the metals and of the alkoxy groups.

It is the purpose of this paper to study the physical properties of the μ -oxoalkoxide complexes in organic solution.

Results

The μ -oxoalkoxides display an amazingly high solubility in most organic solvents and particularly in hydrocarbons (see Experimental). This property can be explained by an intermolecular association giving an aggregate in which a core of μ -oxo bridged metals is surrounded by a lipophilic layer of alkoxy groups. This association obviously results from the tendency of these metals to fulfill their coordination number by forming intra- and intermolecular metal-oxygen bonds, a phenomenon which is already well known for simple metal alkoxides⁵.

The mean degrees of association (\bar{n}) of the μ -oxoalkoxides are measured by cryoscopy in benzene and cyclohexane with a good accuracy and reproducibility. The results are shown in Table I. As expected, it is observed that \bar{n} strongly depends on the nature of the metals, the alkoxy groups and the solvent. Moreover, the μ -oxoalkoxides are systematically less associated in benzene, a behaviour which is probably due to the coordination power of this solvent.

In addition, within the concentration range studied, \bar{n} remains independent of the concentration (within limits of experimental errors). Nevertheless, such a behaviour is not observed for the $\text{ZnO}_2\text{Al}_2(\text{On-C}_4\text{H}_9)_4$ and $\text{FeO}_2\text{Al}_2(\text{On-C}_4\text{H}_9)_4$ compounds for which \bar{n} clearly depends on the concentration of the solution and also on the method of preparation.

TABLE I. Molecular Association of Bimetallic μ -Oxoalkoxides, $(RO)_2Al-O-M^{II}-O-Al(OR)_2$.

M ^{II}	R	Solvent	\bar{n}	Concentration Range Examined <i>M</i>	Colour
Fe ^{II}	iso-C ₃ H ₇	Benzene	1	(0.09–0.2)	Dark Green
		Cyclohexane	2.1	(0.06–0.12)	Dark Green
	n-C ₄ H ₉	Benzene	1–3	} variable with concentration	Dark Green
		Cyclohexane	2–8		Dark Green
	sec-C ₄ H ₉	Benzene	1.1	(0.06–0.10)	Dark Green
		Cyclohexane	2.0	(0.08–0.14)	Dark Green
ter-C ₄ H ₉	Benzene	1.1	(0.04–0.08)	Dark Green	
	Cyclohexane	4.1	(0.04–0.06)	Dark Green	
Co ^{II}	iso-C ₃ H ₇	Benzene	2.0	(0.3–0.6)	Violet-Red
		Cyclohexane	3.0	(0.02–0.1)	Violet-Red
	n-C ₄ H ₉	Benzene	4.1	(0.2–0.8)	Blue
		Cyclohexane	6.2	(0.02–0.12)	Blue
Mo ^{II}	iso-C ₃ H ₇	Benzene	1.1	(0.08–0.8)	Deep Red
		Cyclohexane	2.1	(0.09–0.18)	Deep Red
	n-C ₄ H ₉	Benzene	3.0	(0.18–0.35)	Deep Green
Cr ^{II}	iso-C ₃ H ₇	Benzene	1.1	(0.05–0.12)	Blue
		Cyclohexane	2.0	(0.05–0.08)	Blue
Zn ^{II}	n-C ₄ H ₉	Benzene	4–8	} variable with concentration	Pale Yellow
	sec-C ₄ H ₉	Benzene	4–8		Pale Yellow

On the other hand, we have also studied other structural properties of these compounds in solution and in vapour phase.

Colour and Visible Absorption Spectra

The electronic absorption spectra of these compounds also strongly depend on the molecular association. The visible spectra exhibit two bands at 375 and 490 nm for the MoO₂Al₂(Oiso-C₃H₇)₄ compound and only one distinct absorption band at 750 nm for the MoO₂Al₂(On-C₄H₉)₄ compound (Fig. 1). Moreover, these absorption bands are not dependent on the nature of the solvent and can thus be attributed to electronic transitions between molecular orbitals which have predominantly metal *d* orbital character.

An additional interesting feature is the striking difference in extinction coefficients between these two different compounds (Fig. 1) (see below).

These results indicate the great influence of the nature of the alkoxy groups on the *d*-metal orbitals splitting and consequently on the electronic visible transitions which affect the colour of the complexes (Table I).

NMR Spectra

Figure 2 shows the proton-decoupled ¹³C NMR spectrum of the MoO₂Al₂(Oiso-C₃H₇)₄ compound

which is non-associated ($\bar{n} \approx 1$) in benzene (table I). Two peaks are observed at 26.0 and 28.4 ppm (from TMS) which can be attributed to two different CH₃ groups, as well as two other peaks at 63.6 and 69.2 ppm attributed to CH groups.

This spectrum clearly indicates the presence of two different isopropoxy groups in this compound: two peaks (28.4 and 69.2 ppm) correspond to the carbon atoms of the bridging isopropoxy groups (weak field values), and the others to the carbon atoms of the non-bridging groups (high field values).

The NMR spectrum of this mononuclear species is very simple, and this method is thus very convenient for the study of the intramolecular coordination of the alkoxy groups. On the opposite, the proton-decoupled ¹³C NMR spectra of the polynuclear species are more complex. In the case of ZnO₂Al₂(Osec-C₄H₉)₄ for which \bar{n} is greater than one (Table I), we can also observe the peaks expected for the different carbon atoms of the molecule (Fig. 3). Nevertheless, they are not simple and, for the CH peak, we observe again two distinguishable sec-butoxy groups in the molecule, although the phenomenon is less marked for the other resonance peaks. This result indicates also the presence of bridging and non-bridging isobutoxy groups.

However, from these sole observations, it is unfortunately not possible to distinguish the inter- and the intramolecular bridging groups.

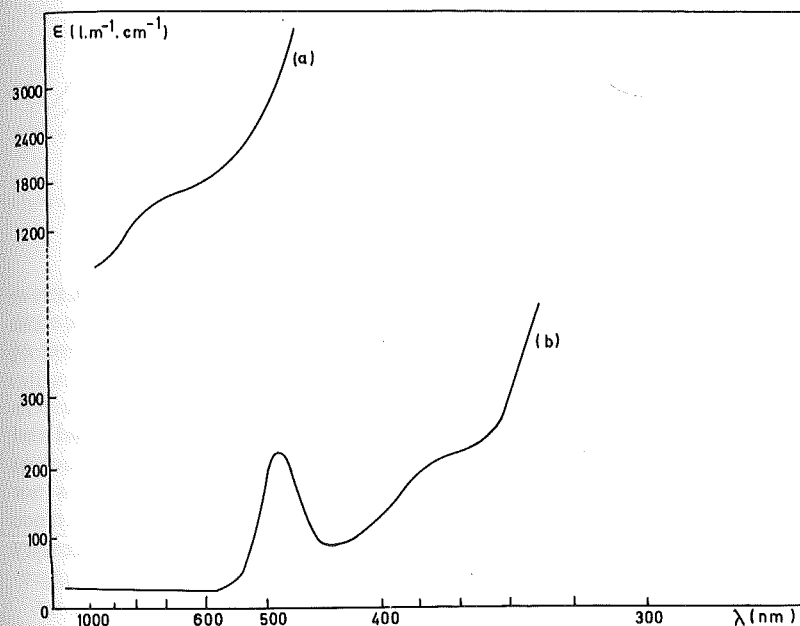
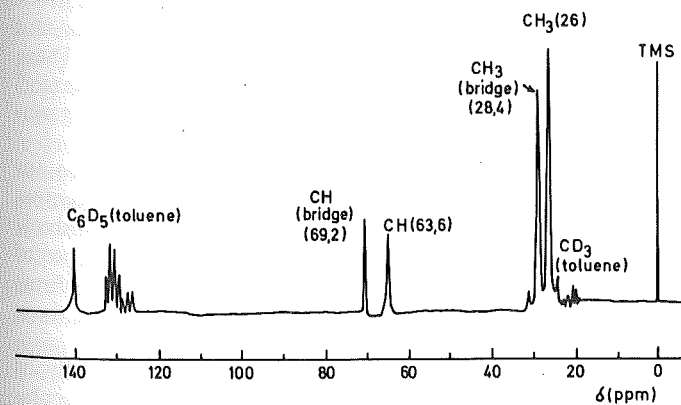
Mass Spectrometry

The molecular association of the μ -oxoalkoxides, in the vapour phase, has also been explored by mass spectrometry. Molecular ion peaks have been observed at *m/e* = 292, 336, 351, 395 and 454, with important relative intensities, for the FeO₂Al₂(Oiso-C₃H₇)₄ compound. These peaks correspond to aggregate fragments which have lost a propene molecule from one of the isopropoxy groups. Such fragmentation schemes have also been observed for Al(Oiso-C₃H₇)₃⁶. The results, quoted in Table II, confirm the intermolecular coordinations between oxygen and metal atoms in the vapour

TABLE II. Molecular Ion Peaks of the FeO₂Al₂(Oiso-C₃H₇)₄ Complex.

Observed <i>m/e</i> Values	Aggregate Fragment	Relative Abundance ^a
292	Fe(Oiso-C ₃ H ₇) ₄	30
336	FeO ₂ Al ₂ (OH)(Oiso-C ₃ H ₇) ₄	45
351	Fe(Oiso-C ₃ H ₇) ₅	59
395	FeO ₂ Al ₂ (OH)(Oiso-C ₃ H ₇) ₄	28
454	FeO ₂ Al ₂ (OH)(Oiso-C ₃ H ₇) ₅	10

^a Estimated with respect to the C₃H₇⁺ peak, taken equal to 100.

Figure 1. Electronic spectra of MoO₂Al₂(OR)₄ in cyclohexane. a) R = n-butyl $1.25 \times 10^{-3} M$; b) R = isopropyl $10^{-2} M$.Figure 2. ¹³C NMR spectrum of MoO₂Al₂(Oiso-C₃H₇)₄.

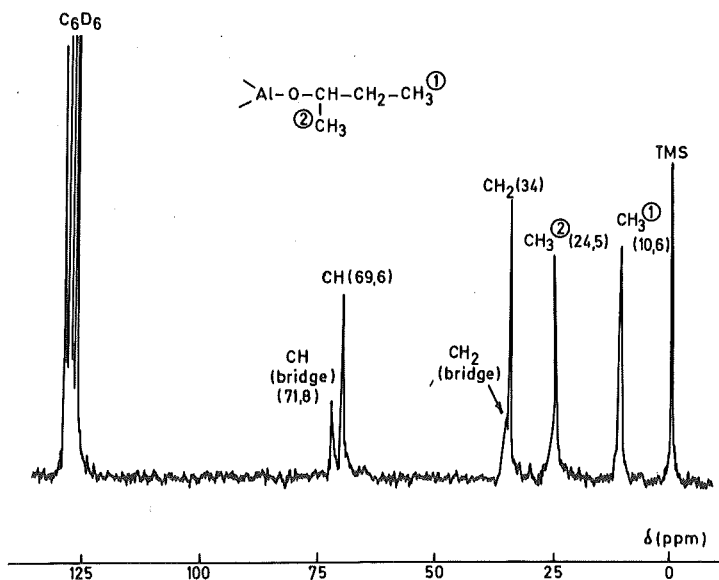


Figure 3. ^{13}C NMR spectrum of $\text{ZnO}_2\text{Al}_2(\text{Osec-C}_4\text{H}_9)_4$.

phase, and can be correlated with the previous observations made on solutions.

Discussion

From the results gathered in Table I, the most interesting conclusion is that the mean degree of association (\bar{n}) depends on the nature of the alkoxy groups: of course, the strength of the metal-oxygen bonds increases with the basicity of the alkoxy groups; but on the other hand, this tendency is opposed by steric factors, which increase as the size of the alkoxy groups increases. The value of \bar{n} depends accordingly on the relative importance between basicity and steric effects, as it has already been observed for simple metal alkoxides⁵.

As might be expected, the degree of molecular association is also directly dependent on the nature and the coordination number of the central metal atom M^{II} . However, this latter parameter is controlled by the nature of the alkoxy groups: their effect on the geometry and the molecular energy levels of the complex is strongly marked, for example by the different colours and electronic absorption spectra of both $\text{MoO}_2\text{Al}_2(\text{Oiso-C}_3\text{H}_7)_4$ and $\text{MoO}_2\text{Al}_2(\text{On-C}_4\text{H}_9)_4$ compounds. Moreover, the high intensity of the $\text{MoO}_2\text{Al}_2(\text{On-C}_4\text{H}_9)_4$ compound can be related to an electronic delocalization in this molecular aggregate. Such ascertaining has been made by different authors which have studied the electronic spectra of strongly delocalized polynuclear compounds⁷.

Finally, the nature of the solvent has also a great importance: the lower values of \bar{n} observed in benzenic solution are probably due to the coordination power of this solvent.

The NMR spectra of polynuclear aggregates are very complex, since the peaks corresponding to bridged and non-bridged alkoxy groups are due to the presence of both inter- and intramolecular interactions: it is not possible at present to estimate the relative importance of both interactions and further studies are necessary to propose detailed molecular models for these aggregates.

Within the temperature and the concentration ranges quoted in Table I, we observe that the mean degree of association of these compounds remains generally independent of the concentration. Moreover, these values are generally close to integers and this is probably due to the predominance of one well-defined and thermodynamically favoured species in solution. These effects are consistent with those reported by Mazzei⁸ for poly(N-alkyliminoalanes) and Owens⁹ for organo-aluminum compounds.

Nevertheless, in some cases, the values of \bar{n} are not close to integers and are dependent on the concentration of the solution and of the method of synthesis (Table I). This result implies probably the existence of different species which are in equilibrium and confirms the great complexity of the overall structure of these μ -oxoalkoxides.

In conclusion, it appears that this new family of coordination compounds, mostly present as molecular aggregates in organic solution, can be compared to small fragments of mixed oxides (formally similar to

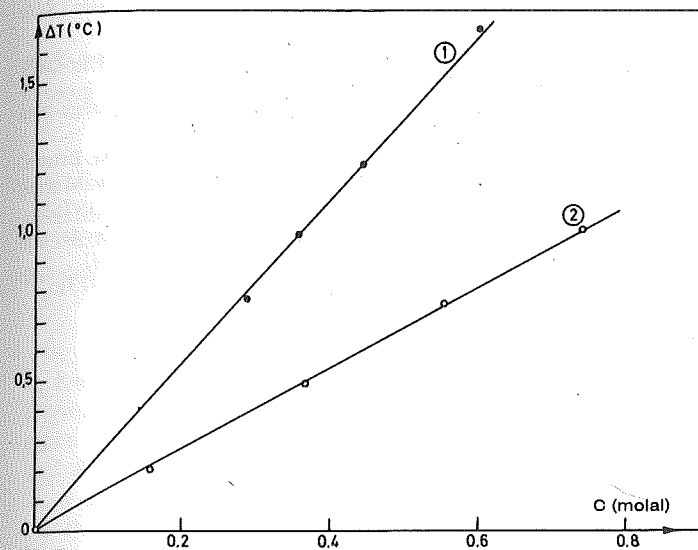


Figure 4. Degree of association of $\text{CoO}_2\text{Al}_2(\text{OR})_4$ in benzene. 1) R = isopropyl; 2) R = n-butyl.

spinels when $\bar{n} = 4$), solubilized by a lipophylic layer of alkoxy groups. As such, they enjoy interesting physical properties characteristic of oxides with electronic delocalization, but they also represent an attractive frontier model between homogeneous and heterogeneous catalysis: this latter aspect will be developed in future publications.

Experimental

All solvents were dried over LiAlH_4 or CaH_2 before distillation, and the experiments were performed under inert atmosphere (argon).

The preparation of the μ -oxoalkoxide compounds was described in details elsewhere².

These complexes are very soluble in most organic solvents. In fact, several of them (for which the alkyl group contains four or more carbon atoms) are practically miscible to alkanes or benzene in every proportion. For instance, a perfectly clear solution is obtained from 10 gr of $\text{ZnO}_2\text{Al}_2(\text{On-C}_4\text{H}_9)_4$ and 8 ml of n-heptane. Moreover, the solubility decreases for smaller alkoxy groups; for instance, the isopropoxy compounds are less soluble than the butoxy ones.

The mean degrees of association (\bar{n}) were determined in a cryometer conceived to operate under an argon atmosphere, and the solutions were injected in the apparatus with hypodermic syringes through a septum. \bar{n} was obtained from the slope of the graph ΔT versus molal concentration C ($\Delta T = K C/\bar{n}$ where the cryoscopic constant of the solvent, $K = 5.1$ and 20.5 for benzene and cyclohexane, respectively) (Fig. 4).

The ^1H and ^{13}C NMR spectra were recorded on Varian (T 60) and Brücker (HFX 90) spectrometers with TMS as internal reference, using 0.3 M solutions in perdeuterated benzene or toluene.

Visible absorption spectra of the compounds in benzene, toluene and cyclohexane solutions were recorded on a Zeiss apparatus (the concentrations of the solutions are quoted in Figure 1), and the mass spectra on an Itachi-Perkin Elmer RMU-6 D spectrometer.

Acknowledgments

Support of this work by the Institut Français du Pétrole is gratefully acknowledged. Two of us (J.P. Bioul and C. Stevens) are respectively indebted to IRSIA and TEXACO for a fellowship. Thanks are due to Prof. A.J. Hubert for helpful discussions, and to Dr. A. Revillon (C.N.R.S., Villeurbanne, 69626, France) for assistance with the synthesis of the chromium complexes. We are also grateful to the Laboratory of Organic Chemistry, University of Brussels, for recording the mass spectra.

References

- 1 a) K.S. Murray, *Coord. Chem. Rev.*, 12, 1 (1974).
- b) W.T. Griffith, *Coord. Chem. Rev.*, 5, 459 (1970).
- c) B. Jezowska-Trzebiatowska and W. Wojciechowski, *Trans. Metal Chem.*, 6, 1 (1970).
- d) P.W. Ball, *Coord. Chem. Rev.*, 4, 361 (1969).

- 2 a) T. Ouhadi, *Ph. D. Thesis*, University of Liège, 1973.
 b) J.P. Bioul, *Ibid.*
- 3 a) A. Hamitou, R. Jérôme, A.J. Hubert and Ph. Teyssié, *Macromolecules*, **6**, 651 (1973).
 b) Ph. Teyssié, T. Ouhadi and J.P. Bioul, *Intern. Rev. of Sci. (Makromol. Sci.) Physical Chem.; Ser. 2, Vol 8*, 191 (1975), Butterworths Ed.
- 4 a) T. Ouhadi, A.J. Hubert, Ph. Teyssié and E. G. Derouane, *J. Am. Chem. Soc.*, **95**, 6481 (1973).
 b) L. Hocks, T. Ouhadi and Ph. Teyssié, in preparation.
- 5 a) D.C. Bradley, *Adv. in Inorg. Chem. and Radiochem.*, **15**, 259 (1972).
 b) R.C. Mehrotra, *Inorg. Chim. Acta Rev.*, **1**, 99 (1967).
- c) R.C. Mehrotra and A. Mehrotra, *Inorg. Chim. Acta Rev.*, **5**, 127 (1971).
- 6 W. Fieggen, H. Gerding and NMM Nibbering, *Rec. Trav. Chim.*, **87**, 377 (1968).
- 7 a) H.J. Schugar, G.R. Rossman, C.G. Barraclough and H.B. Gray, *J. Am. Chem. Soc.*, **94**, 2683 (1972).
 b) T.R. Weaver, T.J. Meyer, S.A. Adeyemi, G.M. Brown, R.P. Eckberg, W.E. Hatfield, E.C. Johnson, R.W. Murray and D. Untereker, *J. Am. Chem. Soc.*, **97**, 3039 (1975).
- 8 S. Cucinella, T. Salvatori, C. Busetto, G. Perego and A. Mazzei, *J. Organometal. Chem.*, **78**, 185 (1974).
- 9 R.M. Owens, *J. Organometal. Chem.*, **55**, 237 (1973).

Cation Distribution in Spinels: Lattice Energy versus Crystal Field Stabilisation Energy

C. GLIDEWELL

Chemistry Department, University of St. Andrews, Fife, KY16 9ST, Scotland, U.K.

Received April 15, 1976

Ever since the discussions by McClure¹ and by Dunitz and Orgel,² the observed distributions of metal cations between the octahedral and tetrahedral sites in spinels AB₂O₄ have been regarded as a classic exemplar of the chemical significance of crystal field stabilisation energy (CFSE).

Although it is to be expected that the normal spinels will have lattice energies different from the corresponding inverse spinels, neither of these papers^{1,2} makes any quantitative assessment of the change in lattice energy on inversion, and indeed McClure effectively dismisses this as unimportant, largely on the grounds that, of the examples he cites, the structure of the majority for which the CFSE is non-zero are correctly predicted by the CFSE alone, even though *no* CFSE prediction can be made for about one-third of his examples: of these, some are normal and some inverse. Navrotsky and Kleppa³ also dismissed the change in lattice energy as essentially unimportant.

Calculations have since been made⁴⁻⁶ of the Madelung constants of cubic spinels in terms of the lattice parameter *a*, the degree of inversion λ ($\lambda = 0$ for normal, 0.5 for inverse), and the anion displacement parameter δ : in an ideal spinel having close packed anions, the fractional coordinate *x* of the anions at positions 32_e in space group *Fd3m* is 0.375, and in non-ideal spinels $\delta = x_{\text{obs}} - 0.375$. Observed values of δ range from -0.003 in MgIn₂O₄⁷ to +0.017 in MgGa₂O₄⁸ and in HgCr₂S₄⁹ amongst the 2-3 spinels, and from zero in SnCo₂O₄¹⁰ and MoFe₂O₄¹¹ to +0.015 in TiFe₂O₄,⁷ TiMg₂O₄⁷ and SnZn₂O₄¹⁰ amongst the 4-2 species (Mössbauer spectra indicate¹² that tin spinels contain Sn(IV) rather than Sn(II)). These extreme values of δ correspond to changes in Madelung energy on inversion, M(normal) - M(inverse) of +525.8 kJ mol⁻¹ in MgIn₂O₄ and -1071.6 kJ mol⁻¹ in MgGa₂O₄ as the extreme 2-3 examples, and of -1400.3 kJ mol⁻¹ in MoFe₂O₄ and +270.5 kJ mol⁻¹ in TiMg₂O₄ as the extremes amongst 4-2 species.

In view of the availability of Madelung constants for spinels, it seems worthwhile to reconsider the distribution of cations in those species AB₂X₄ (X = O, S, Se, Te) for which δ is known, in terms of the

changes on inversion in both CFSE and Madelung energy.

In the Table are listed values of $\Delta U = U(\text{normal}) - U(\text{inverse})$, $\Delta(\text{CFSE}) = \text{CFSE}(\text{normal}) - \text{CFSE}(\text{inverse})$, and the total stabilisation energy of the normal form with respect to the inverse. ΔU values were calculated,⁴⁻⁶ using *n* = 9 as the exponent of the Born repulsion term, from the observed values of *a* and δ , structural data, except where otherwise noted, being taken from Wyckoff.¹³ CFSE values were calculated,¹⁴ assuming for the Racah parameters that *C* = 4*B*, using *f*, *g*, and *B* data given by Jorgensen,^{15,16} and estimated *g* factors as follows: Cr(II), 10.0; Mn(III), 21.0; Cu(II), 9.5; Mo(IV), 30.0; *f* for S⁻² was taken as 0.89,¹⁵ and similar values were adopted for Se⁻² and Te⁻².

Of the twenty-two 2-3 oxides listed in the Table, the predicted structure is observed for fifteen: of those incorrectly predicted, the calculated total energy change on inversion is small for CuFe₂O₄ (-20.9 kJ mol⁻¹) and for NiFe₂O₄ (-50.6 kJ mol⁻¹), so these discrepancies are probably not significant. The remaining five are all predicted to be normal but observed to be inverse: similarly, amongst the 4-2 oxides SnCo₂O₄ and TiZn₂O₄ are found to be inverse, although predicted to be normal (the structure of NiMn₂O₄ is probably¹⁷ Mn^{II}(Ni^{III}, Mn^{III})₂O₄, rather than Mn^{III}(Ni^{II}, Mn^{III})₂O₄, and so is normal, with M(II) in the tetrahedral site).

There are several plausible explanations for the discrepancies. Firstly, the Madelung energy and its change on inversion are very sensitive to the anion displacement parameter δ and hence to *x*. Most spinels have values of δ around +0.010 (*i.e.* *x* = 0.385): for such a spinel of cell length *a* = 8.5 Å, a change of ± 0.001 in *x* represents a change in ΔU on inversion of *ca.* 92.5 kJ mol⁻¹ for 2-3 species and of *ca.* 97.0 kJ mol⁻¹ for 4-2 species. Consequently an experimental uncertainty of ± 0.001 in *x* will lead to an uncertainty in ΔU which is greater than $\Delta(\text{CFSE})$ for all species except those containing Cr(III) or Mo(IV), and in many examples it is probable that the experimental uncertainty in *x* is of this magnitude.

Secondly there is the question of oxidation states: the example of NiMn₂O₄ has already been mentioned. In the case of CuMn₂O₄, it has been suggested¹⁸ that this compound is not a simple Mn(III) species but should be formulated as (Cu^I_{1-p}Mn^{II}_{1-p})₂(Cu^I_{1-p}Mn^{IV}_{1-p}Mn^{III}_{2p})₂O₄ (with 0 < *p* < 0.33), whose lattice energy cannot easily be calculated. In MnFe₂O₄, the manganese ions suffer oxidation on transference to the octahedral sites¹⁹ and the constitution is more properly described as (Mn^{II}_pFe^{III}_{1-p})₂(Fe^{II}_{1-p}Mn^{III}_{1-p}Fe^{III}_{2p})₂O₄, having *p* = 0.81; other examples of this type of behaviour are¹⁷ CoMn₂O₄ and FeMn₂O₄. A different phenomenon occurs in FeFe₂O₄; below