SYNTHESIS, STRUCTURAL AND MAGNETIC STUDIES OF IMIDAZOLIUM BIS(OXALATO)CUPRATE(II)

SHYAMAL K. CHATTOPADHYAY

Department of Chemistry, Bengal Engineering College (Deemed University),
Howrah 711103, India

THOMAS C. W. MAK and BAO-SHENG LUO

Department of Chemistry, The Chinese University of Hong Kong, Shatin,
New Territories, Hong Kong

LAURENCE K. THOMPSON

Department of Inorganic Chemistry, Memorial University of Newfoundland,
St. John's, Newfoundland, Canada A1B 3X7

and

ARINDAM RANA and SAKTIPROSAD GHOSH*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta 700 032, India

Abstract—Imidazolium bis(oxalato)cuprate(II) has been synthesized and its structure determined by X-ray crystallography. Variable temperature magnetic susceptibility measurements, as well as EPR and UV–vis spectroscopic studies, have been carried out. The results show that in the solid state the compound exists in a chain-like structure, with an asymmetric one-atom weak oxalate bridge joining adjacent Cu^{II} centres. Of the two oxygen atoms of each coordinated oxalate, only one participates in bridging; thus, each oxalate ultimately achieves three-point coordination. Each of the imidazolium ions participates in two hydrogen bonds through the two N—H moieties. The compound exhibits a weak antiferromagnetic interaction ($J = -0.40$ cm^{-1}). EPR spectra reveal that the triplet state is appreciably populated at both room and liquid nitrogen temperatures.

The chemistry of carboxylate-bridged copper complexes has been an active area of investigation[1-10] over the years, because of their particularly interesting magnetic properties. Among the different types of bridging carboxylates, oxalato bridged complexes are currently the most actively studied,[6-9] because they can be used to prepare compounds with predictable magnetic properties. A variety of co-ligands were used to tailor the coordination geometry and the relative orientation of magnetic orbitals of the bridged copper ions. However, relatively little is known about the systems in which copper is coordinated to two oxalate ions, presumably constituting a square plane. Knowledge about such a system could throw more light on how a co-ligand affects magnetic exchange through the oxalate bridge. The only known compound where such a situation is believed to exist is "copper oxalate", which exhibits[3] anomalous magnetic behaviour. However, no structural data on this compound are available and all reported attempts

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*Author to whom correspondence should be addressed.

to crystallize it have been unsuccessful.[2,3] The title compound was obtained in an attempt to prepare the imidazole derivative of copper oxalate, in the hope of obtaining a more soluble compound which might yield good single crystals suitable for structural characterization. There was also a finite possibility that the coordinated imidazole might change the relative orientation of magnetic orbitals of adjacent copper ions and might significantly alter the magnetic behaviour of "copper oxalate".

EXPERIMENTAL

Chemicals

Oxalic acid and basic copper(II) carbonate were obtained from Aldrich. Imidazole was obtained from Fluka. All other chemicals were from Merck (Germany) or E. Merck (India).

Preparation

"Copper oxalate" was prepared by a similar procedure as described earlier[10] for copper malonate. To a suspension of 1.5 g of copper oxalate in 150 cm^3 distilled water, about 3 g of oxalic acid was added and the solution was heated on a water bath for 45 min. To this hot solution 1.15 g of imidazole was added slowly over a period of 15 min, with continuous stirring. The colour of the solution changed to sky blue. It was then heated on a water bath for another 30 min. The pH of the solution was observed to be between 3 and 4. It was filtered hot. On slow cooling of the filtrate, prism-shaped blue crystals separated out. These were filtered off, washed with cold water and dried over fused calcium chloride. Found: C, 31.8; N, 14.4; H, 2.6; Cu, 16.7. Calc. for $C_{10}H_{10}CuN_4O_8$: C, 31.8; N, 14.8; H, 2.6; Cu, 16.8%.

Physical measurements

Carbon, nitrogen and hydrogen analyses were performed on a Perkin–Elmer 240 C, H, N analyser. Copper was determined volumetrically by the iodide–thiosulphate method, after decomposition of the complex by nitric acid. IR spectra were recorded on a Perkin–Elmer 783 Spectrometer using a KBr pellet of the compound. Electronic spectra were recorded on a Jasco UV–vis spectrophotometer. TG–DTA measurements were carried out on a Shimadzu DT30 thermal analyser. Static magnetic susceptibility measurements in the range 300–4.5 K were carried out using an Oxford Instruments Superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. Sus-ceptibility data were corrected for Pascal's diamagnetic correction and for temperature-independent paramagnetism. Hg[Co(NCS)$_4$] was used as a calibrant standard. EPR spectra were obtained on a Varian E-4 X-band spectrometer using diphenylpicryl hydrazyl (dpph) as an internal marker. Cyclic voltammetry was carried out in double distilled water, with a BAS CV-27 instrument, coupled with an X–Y recorder, using a platinum working electrode, a platinum wire auxiliary electrode, Ag/AgCl as reference electrode and TEAP as supporting electrolyte.

Crystallography

Crystal data. $C_{10}H_{10}CuN_4O_8$; $M = 377.8$, triclinic, space group $P\bar{1}$, $a = 3.669(1)$; $b = 9.422(2)$; $c = 10.074(2)$ Å, $\alpha = 106.81(2)°$, $\beta = 97.77(2)°$, $\gamma = 94.02(2)°$, $U = 328.15(11)$ Å^3. Unit cell parameters were calculated from least square fitting of $2\bar{\theta}$ angles for 25 selected strong reflections; λ(Mo-K_α) = 0.71073 Å. $D_M = 2.010$, $Z = 1$, $D_c = 1.912$ g cm^{-3}, blue prism-shaped crystal, 0.1 × 0.20 × 0.28 mm^3, μ(Mo-K_α) = 1.72 mm^{-1}, $F(000) = 191$.

Data collection and processing. 1163 reflections were measured (all of which were unique) on a Siemens R3m/V diffractometer using graphite mono-chromated Mo-K_α radiation using the ω–2θ mode in the range $3° < 2\theta < 50°$, covering indices h: 0–4; k: -11 to $+11$; l: -11 to $+11$. Crystal stability was monitored by recording two check reflections at intervals of 123 reflections. No significant variation in the intensity of these monitoring reflections was observed. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure analysis and refinement. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. Using 1129 observed reflections ($|F_0| \geqslant 4\sigma$ ($|F_0|$), refinement converged ($\Delta/\sigma \approx 10^{-4}$) with $R = 0.0267$, $R_w = 0.036$. For all reflections $R = 0.0274$ and $R_w = 0.036$. The weighing scheme was $w = (\sigma^2(F) + 0.00005\ F^2)^{-1}$. Goodness of fit $S = 2.76$.

In a final difference Fourier map the maximum and minimum peaks were 0.59 and -0.26 e Å^{-3}, respectively.

All calculations were carried out on a DEC Microvax-II computer using the SHELXTL-PLUS programme package.[11] Analytical expressions of neutral atom scattering factors were employed and dispersion corrections incorporated.[12]

RESULTS AND DISCUSSION

Description of the crystal structure

An ORTEP plot of one asymmetric unit is presented in Fig. 1, which also shows the atom labelling scheme. From the figure it is clear that the Cu(1) atom adopts a 4+2 coordination geometry, with approximately D_{2h} site symmetry. The two carboxylate oxygens of each oxalate moiety chelate the Cu^{II} acceptor centre, resulting in the formation of a five-membered ring. The four oxygen atoms (O(1), O(4), O(1a) and O(4a)] of these two chelated oxalate moieties constitute a square plane (plane 1)

with Cu(1) at its centre. The in-plane Cu—O distances are found to be equal (Table 1) and in close agreement with those reported for other copper oxalate complexes.[7,9] Similarly, the rather small O(1)—Cu(1)—O(4) angle (85.2°) is also in agreement with that reported in previous works.[7,9] Besides these four in-plane symmetrical Cu(1)—O bonds, Cu(1) is also coordinated by two very long axial bonds (Cu—O distance 2.875 Å) to two other carboxylate oxygens, each chelated to a different Cu^{II} unit lying above and below the square plane containing Cu(1) [Cu(1e) in Fig. 1], the Cu^{II} units being related to Cu(1) by lattice translation. These two Cu^{II} centres, in turn, have one of their apical
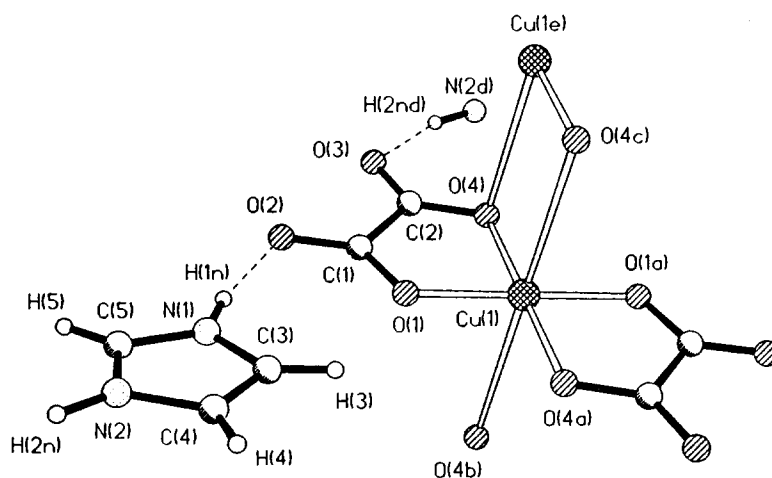

Fig. 1. Perspective view showing the coordination geometry about the Cu^{II} atom, details of the hydrogen bonding and the atom numbering.

Table 1. Bond lengths (Å) and bond angles (°)

Cu(1)—O(1)	1.931(2)		Cu(1)—O(4)	1.932(2)	
Cu(1)—O(4b)	2.875(3)		O(1)—C(1)	1.278(3)	
O(2)—C(1)	1.229(2)		O(3)—C(2)	1.229(3)	
O(4)—C(2)	1.278(2)		C(1)—C(2)	1.555(3)	
N(1)—C(3)	1.370(3)		N(1)—C(5)	1.313(3)	
C(3)—C(4)	1.333(4)		C(4)—N(2)	1.367(3)	
N(2)—C(5)	1.319(4)		O(2)···N(1)	2.761(5)	
O(3)···N(2d)	2.772(5)				
O(1)—Cu(1)—O(4)	85.2(1)		O(1)—Cu(1)—O(4b)	86.2(1)	
O(4)—Cu(1)—O(4c)	82.4(1)		Cu(1)—O(1)—C(1)	112.7(1)	
Cu(1)—O(4)—C(2)	112.7(2)		O(1)—C(1)—O(2)	125.9(2)	
O(1)—C(1)—C(2)	114.5(2)		O(2)—C(1)—C(2)	119.6(2)	
O(3)—C(2)—O(4)	125.5(2)		O(3)—C(2)—C(1)	120.0(2)	
O(4)—C(2)—C(1)	114.4(2)		C(3)—N(1)—C(5)	109.0(2)	
N(1)—C(3)—C(4)	107.0(2)		C(3)—C(4)—N(2)	106.9(2)	
C(4)—N(2)—C(5)	109.0(2)		N(1)—C(5)—N(2)	108.1(2)	
N(1)—H(1N)···O(2)	166.0(3)		N(2d)—H(2Nd)···O(3)	165.9(3)	

Symmetry transformations: a $(-x, -y, -z)$; b $(1+x, y, z)$; c $(-1-x, -y, -z)$; d $(-1+x, 1+y, z)$; e $(-1+x, y, z)$.
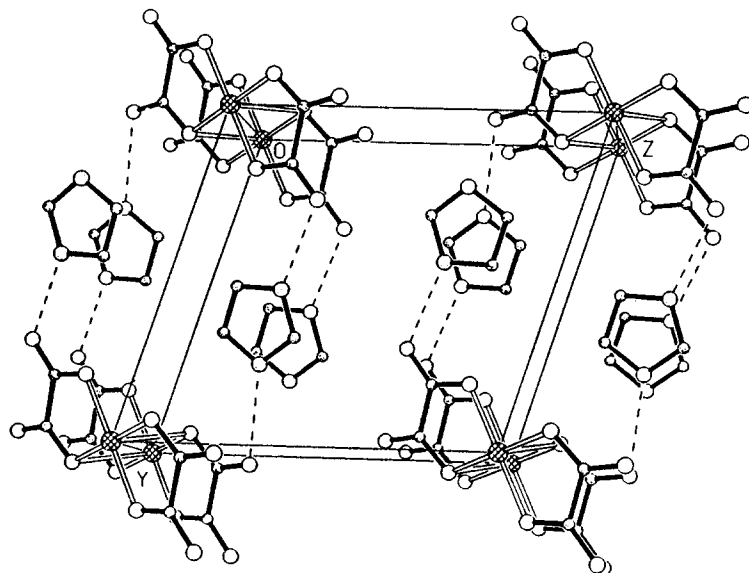
Fig. 2. Crystal structure of $(ImzH)_2[Cu(C_2O_4)_2]$. The origin of the unit cell lies at the upper left corner, with a pointing towards the reader, b downward at a slant and c from left to right. Hydrogen bonds of the type N—H$\cdots$O are represented by broken lines.

positions occupied by O(4) and O(4a), respectively, through a long Cu—O bond. In this way, two carboxylate oxygens of each oxalate behave differently with respect to coordination to Cu^{II} centres, with only one of them being involved in bridging. This is definitely the most important feature of this structure, as one-atom carboxylate bridging is quite rare.[13]

All the four oxygen atoms of the four different oxalates [O(4), O(4a), O(4b) and O(4c)] form a plane (plane II) with Cu(1) at the centre, which is at 86.2° to plane I [O(1), O(4), Cu(1), O(1a), O(4a)]. These four oxygen atoms (forming plane II) are again related through lattice translation, though Cu—O bonds in this plane are not identical [Cu(1)—O(4) = 1.932 Å, Cu(1)—O(4b) = 2.875 Å]. The distortion around Cu(1) can be expressed in terms of its rather low tetragonality factor[14] $T = 0.67$ ($T = R_S/R_L$, R_S = mean in-plane Cu—O distance, R_L = mean out-of-plane Cu—O distance).

All the oxygen atoms of a given oxalate [e.g. O(1), O(2), O(3), O(4)] also form a plane (plane III) and the dihedral angle between planes I and III is quite small (5.36°). The small dihedral angle favours electron delocalization throughout the $Cu(C_2O_4)^{-2}$ moiety, resulting in a Cu—O bond length which is in the lower side of the range[15] (1.92–2.16 Å) for similar bonds in copper carboxylate complexes.

The protonated imidazole moiety is planar (plane IV) and the angle between planes III and IV is

138.16°. The bond length and bond angles of the imidazolium moiety are similar to those reported elsewhere.[16] Each of the oxalate moieties is involved in hydrogen bonding with the imidazolium ion. Each imidazolium unit, on the other hand, is involved, with its two N—H moieties hydrogen bonding with two carbonyl oxygen atoms of two different oxalate moieties chelated to two Cu^{II} centres in successive planes.

IR spectra

The IR spectra of the compound exhibit two sharp bands at 3158 and 3118 cm^{-1} corresponding to v(N—H) of the imidazolium ion and at 1600 cm^{-1} corresponding to δ(N—H) of the same ion. The coordinated oxalate exhibits a number of characteristic vibrations[17] e.g. 1700 and 1665 cm^{-1} [v_{as}(C=O)], 1635 cm^{-1} [v_{as}(C—O)], 1415 cm^{-1} [v_s(CO) + v(CC)] etc. A band at 420 cm^{-1} may be assigned to the v(Cu—O) vibration.

TG and DTA study

TG and DTA indicate that the compound is stable up to 170°C. It decomposes sharply beyond 180°C providing a phase that is stable from 190 to 300°C. Thereafter, it again decomposes rather slowly until the CuO phase is reached at about 450°C.

Electronic spectra

In dilute aqueous solution (conc. $\sim 10^{-4}$M), the compound exhibits a number of low intensity ($\varepsilon < 10^3$) transitions at 710 (br), 510, 460, 435 and 390 nm, besides two high intensity ($\varepsilon > 10^4$) charge transfer transitions at 250 and 210 nm. The first four transitions probably correspond to d–d transitions. In D_{2h} symmetry, four d–d transitions are expected,[18] corresponding to the $d_{z^2} \rightarrow d_{x^2-y^2}, d_{xy} \rightarrow d_{x^2-y^2}, d_{xz} \rightarrow d_{x^2-y^2}, d_{yz} \rightarrow d_{x^2-y^2}$ transitions. However, in the absence of a polarized spectrum, correct assignments cannot be made. The band around 390 nm probably corresponds to electron transfer from the highest filled π-non-bonding orbital to the σ-antibonding $d_{x^2-y^2}$ orbital.[3] Similar transitions have been observed for other copper carboxylate complexes.[2,3,10] The bands in the UV region probably correspond to intraligand transitions.

Cyclic voltammetry

On first scan the compound exhibits an oxidation peak at 0.50 V and a broad reduction peak at -0.60 V, both peaks being irreversible. The oxidative peak probably corresponds to Cu^{II}/Cu^{III} oxidation, whereas the broad reduction peak is probably due to overlapping peaks of Cu^{II}/Cu^{I} and Cu^{I}/Cu reductions. On scanning back from the negative side, a new peak appears at $+0.15$ V. The sharpness of the peak, as well as the high peak current, indicates that it probably corresponds to the $Cu \rightarrow Cu^{2+} + 2e^-$ stripping process.

Magnetic susceptibility and EPR spectroscopy studies

Variable temperature magnetic susceptibility measurements down to 4.5 K were made and a $(\chi_M * T)$ vs T plot is given in Fig. 3. From the figure it is clear that there is very little variation of susceptibility with temperature, indicating that the metal centres are very weakly coupled. Fitting the data to the Bleany–Bowers equation[19] by using isotropic (Heisenberg) exchange gives $J = -0.40$ cm^{-1}, with a g value of 2.163 [$ZJ' = 0$, $R = 0.77$; $R = \Sigma \, |\chi_M^{obsd} - \chi_M^{calc}|^2 / \Sigma (\chi_M^{obsd})^2$]. Since the singlet–triplet splitting is comparable with the Zeeman energy $g\beta H$, the data were also fitted to the Friedberg magnetization expression:[20]

$$M = [Ng\beta \sinh (g\beta H/kT)][\exp (|-2J|/kT) + 2\cosh (g\beta H/kT) + 1]^{-1},$$

where $\chi_M = M/H + N$.

A better fit was obtained with $g = 2.159$, $J = -1.09$ cm^{-1} ($ZJ' = 0.05$ cm^{-1}, $R = 0.007$). The average g values compare reasonably well with those obtained from EPR studies (see below).

A weak coupling such as this between the Cu^{II} centres is expected from the structure, as their magnetic orbitals ($d_{x^2-y^2}$) are parallel rather than coplanar and the bridging oxygen atom couples the $d_{x^2-y^2}$ orbital of one Cu^{II} centre with the d_{z^2} orbital (rather than $d_{x^2-y^2}$) of the adjacent Cu^{II} centre. Thus, the geometry of the complex is unfavourable for transmitting exchange coupling. EPR spectra of the powdered sample (Fig. 4) at both room and
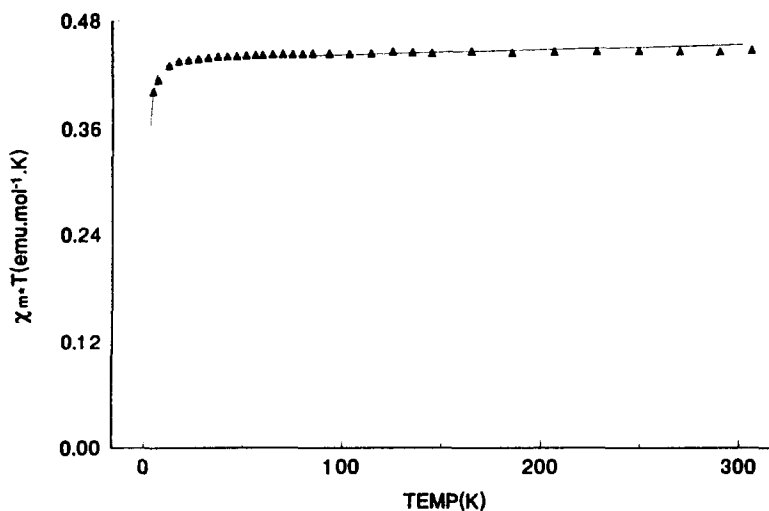

Fig. 3. Thermal variation of susceptibility of the complex in the range 4.5–300 K. ($\triangle$) Experimental data; (-) theoretical curve using Friedberg's expression.
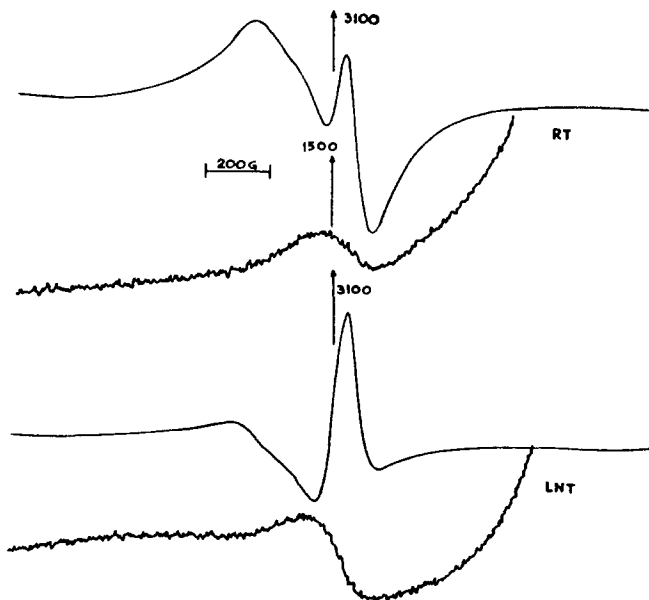
Fig. 4. EPR spectra of the polycrystalline complex at room temperature (a) and liquid nitrogen temperature (b).

liquid nitrogen temperatures consist of a signal at $g = 2.01$ (g_1) and two overlapping broad absorptions at $g = 2.17$ (g_2) and $g = 2.28$ (g_3). There is also a forbidden transition at $g = 2.05$. In addition, at both temperatures a half-field signal corresponding to $\Delta M_s = \pm 2$ is observed, indicating that the triplet state is appreciably populated at both room and liquid nitrogen temperatures. The broadness of the signal may be attributed to dipolar interaction or/and a very weak exchange between equivalent ions.[21]

CONCLUSION

Though a wide variety of mononuclear and binuclear copper complexes with oxalate as the core ligand and a host of different types of co-ligands have been studied, a complete structural characterization of a copper complex containing the oxalate ion as the sole occupant of the coordination sites has not been reported before and, to the best of our knowledge, the present work is the first report of such a case. This compound presents a very unusual situation in which only one of the two oxygen atoms of a chelated oxalate moiety participates in bridging. Magnetic study of this Cu^{II} complex clearly indicates that, unlike doubly bridged oxalato complexes, the adjacent Cu^{II} centres are very weakly coupled and the structure of this compound explains why this is so.

REFERENCES

1. R. D. Willet, D. Gatteschi and O. Kahn (Eds), *Magneto-Structural Correlations in Exchange Coupled Systems*. D. Reidel, Dordrecht (1985).
2. L. Dubicki, C. M. Harris, E. Kokot and R. L. Martin, *Inorg. Chem.* 1966, **5**, 93.
3. B. N. Figgis and D. J. Martin, *Inorg. Chem.* 1966, **5**, 100.
4. M. Kao, H. B. Jonassen and J. C. Fanning, *Chem. Rev.* 1964, **64**, 99.
5. J. Lewis, *Pure Appl. Chem.* 1965, **10**, 27.
6. A. Bencini, C. Benelli, D. Gatteschi, C. Zanchini, A. C. Fabretti and G. C. Franchini, *Inorg. Chim. Acta* 1984, **86**, 169.
7. M. Julve, M. Verdaguer, A. Gleizes, M. Philoche-Levisalles and O. Kahn, *Inorg. Chem.* 1984, **23**, 3808.
8. M. Julve, M. Verdaguer, O. Kahn, A. Gleizes and M. Philoche-Levisalles, *Inorg. Chem.* 1983, **22**, 368.
9. A. Gleizes, M. Julve, M. Verdaguer, J. A. Real, J. Faus and X. Solans, *J. Chem. Soc., Dalton Trans.* 1992, 3209.
10. D. Chattopadhyay, S. K. Chattopadhyay, P. R. Lowe C. H. Schwalbe, S. K. Mazumdar, A. Rana

and S. Ghosh, *J. Chem. Soc., Dalton Trans.* 1993, 913.

11. (a) G. M. Sheldrick, in *Computational Crystallography* (Edited by D. Sayre), p. 506. Oxford University Press, New York (1982). (b) G. M. Sheldrick, in *Crystallographic Computing* 3 : *Data Collection, Structure Determination, Proteins and Databases* (Edited by G. M. Sheldrick, C. Kruger and R. Goddard), p. 175. Oxford University Press, New York (1982).

12. *International Tables for X-ray Crystallography*, Vol. 4. Kynoch Press, Birmingham (1974).

13. A. G. Bingham, H. Bogge, A. Muller, E. W. Ainscough and A. M. Brodie, *J. Chem. Soc., Dalton Trans.* 1987, 493 and references therein.

14. R. J. Dudley and B. J. Hathaway, *J. Chem. Soc. (A)* 1970, 2794.

15. B. J. Hathaway, *Struct. Bonding (Berlin)* 1973, **14**, 49.

16. B. K. Keppler, D. Wehe, H. Endres and W. Rupp, *Inorg. Chem.* 1987, **26**, 844.

17. J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.* 1962, **36**, 324.

18. N. S. Hush and R. J. M. Hobbs, *Prog. Inorg. Chem.* 1968, **10**, 456.

19. B. Bleany and K. D. Bowers, *Proc. R. Soc. Lond. A* 1952, **214**, 451.

20. (a) B. E. Myers, L. Berger and S. A. Friedberg, *J. Appl. Phys.* 1969, **40**, 1149. (b) W. E. Marsh, K. C. Patel, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.* 1983, **22**, 511.

21. J. P. Costes, F. Dahan and J. P. Laurent, *Inorg. Chem.* 1992, **31**, 284.