Synthesis and Structural Studies of Tetraaquacopper(II) Diaquabis(malonato)cuprate(II) †

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Tetraaquacopper(II) diaquabis(malonato)cuprate(II) has been synthesised and its structure determined by X-ray crystallography. Variable-temperature magnetic susceptibility measurements, as well as EPR and UV/VIS spectroscopic studies have also been carried out. The results show that in the solid state the compound exists as a binuclear entity, while in aqueous solution it appears to be mononuclear. This study sets at rest earlier conjectures about the structure of this interesting compound which is also found to exhibit antileukaemic activities *in vivo*.

The chemistry of binuclear copper(II) complexes involving a variety of bridging ligands has been investigated exhaustively aided by a wide variety of physical techniques such as electronic spectroscopy, variable-temperature susceptibility measurements, EPR spectroscopy, *etc.* These physical data can be nicely correlated with structural data, so as to elucidate the nature of electronic and magnetic interactions between copper(II) centres and the way in which these can vary with the nature of bridging groups, coligands, *etc.*[1-8] One such group of compounds which has received much attention are carboxylato-bridged species.[9-14] In this work we report the structural and spectroscopic characterisation of tetraaquacopper(II) diaquabis(malonato)cuprate(II) which contains an unusual type of carboxylate bridge. Copper(II) malonate complexes have been reported by several groups,[11-14] and conjecture about the structure of the species has been based exclusively on variable-temperature magnetic susceptibility data and cannot be regarded as conclusive in the absence of X-ray crystallography. The compound $[Cu(H_2O)_4][Cu\{CH_2(CO_2)_2\}_2(H_2O)_2]$ reported in this work is also found to possess activity against certain tumour cells. Similar activity has been found with (ethylenediamine)malonatoplatinum(II) which is currently undergoing clinical trials as a second-generation antitumour platinum drug.[15]

Experimental

Chemicals.—Malonic acid and basic copper(II) carbonate $CuCO_3 \cdot Cu(OH)_2$ were obtained from Aldrich. All other reagents were obtained from E. Merck (India) and were of reagent grade.

Preparation.—To a suspension of basic copper(II) carbonate (1 g) in water (150 cm^3) in a water-bath was added malonic acid in small portions with stirring, allowing effervescence to subside between subsequent additions. The process was continued until about 20% of basic copper(II) carbonate remained unreacted. The hot reaction mixture was filtered and the solution allowed to evaporate at room temperature when blue crystals of the compound appeared. They were filtered off, washed twice with cold water and then dried over fused calcium chloride (Found: C, 16.30; H, 3.60; Cu, 28.90. Calc. for $C_6H_{16}Cu_2O_{14}$: C, 16.40; H, 3.65; Cu, 28.95%).

Physical Measurements.—Carbon and hydrogen analyses were performed on a Perkin Elmer 240 C,H,N analyser. Copper was determined gravimetrically using α-benzoin oxime.[16] Electronic spectra were recorded on a Shimadzu-UV 2100 spectrophotometer. Infrared spectra were recorded on a Perkin Elmer 783 spectrometer using a KBr pellet of the compound. Static magnetic susceptibility measurements in the temperature range 297–80 K were made using a Curie balance, standardised with $Hg[Co(SCN)_4]$. The effective magnetic moment μ_{eff} was calculated as in ref. 12. Solution conductance was measured with a Philips PR9500 bridge, using a cell calibrated with 0.02 mol dm^{-3} KCl solution. The EPR spectra were obtained on a Varian E-4 X-band spectrometer using diphenylpicrylhydrazyl (dpph) as an internal field marker.

Crystallography.—Crystal data. $C_6H_{16}Cu_2O_{14}$, $M = 439.28$, orthorhombic, space group *Pbcn*, $a = 14.861(2)$, $b = 14.989(2)$, $c = 12.645(2)$, $U = 2815.6(7)$ Å^3 [by least-squares refinement of diffractometer angles for 25 automatically centred reflections; λ(Mo-Kα) = 0.7107 Å], $D_m = 2.10$ g cm^{-3} (by flotation in benzene–bromoform), $Z = 8$, $D_c = 2.07$ g cm^{-3}, blue plate-shaped crystal 0.60 × 0.30 × 0.30 mm, μ(Mo-Kα) = 31.01 cm^{-1} $F(000) = 1778$.

Data collection and processing. 6035 Reflections were measured (of which 2771 were unique) on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation in the range $2 < \theta < 25°$. Scan mode ω–2θ, scan angle $(1.10 + 0.35 \tan \theta)°$. The intensity was checked every 2 h of X-ray exposure time and orientation checked after every 200 reflections. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

Structure analysis and refinement. The structure was solved by Patterson and heavy-atom methods. Full-matrix least-squares refinement of non-hydrogen atoms was carried out first with

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

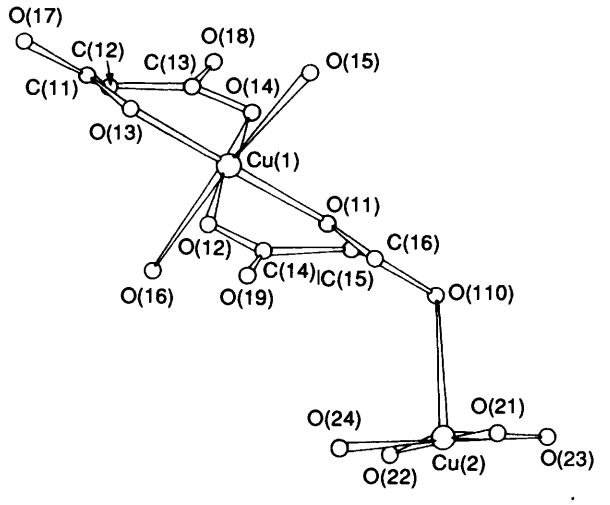

Fig. 1 Atom labelling scheme for tetraaquacopper(II) diaquabis(malonato)cuprate(II)

Table 1 Fractional atomic coordinates for $[Cu(H_2O)_4][Cu\{CH_2(CO_2)_2\}_2(H_2O)_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.249 05(3)	0.105 26(3)	0.258 26(4)
Cu(2)	0.499 86(3)	0.145 05(3)	0.604 51(4)
O(11)	0.361 2(2)	0.085 1(2)	0.334 3(2)
O(12)	0.229 7(2)	0.216 6(2)	0.334 9(2)
O(13)	0.136 2(2)	0.124 9(2)	0.183 5(2)
O(14)	0.269 6(2)	−0.005 9(2)	−0.183 0(2)
O(15)	0.332 1(3)	0.187 8(3)	0.126 5(3)
O(16)	0.164 8(3)	0.020 2(3)	0.397 8(3)
O(17)	0.016 6(2)	0.083 3(2)	0.094 1(3)
O(18)	0.226 8(2)	−0.134 8(2)	0.116 9(3)
O(19)	0.274 9(2)	0.343 9(2)	0.402 8(3)
O(110)	0.484 6(2)	0.125 7(2)	0.417 5(3)
O(21)	0.560 8(2)	0.258 4(2)	0.595 4(3)
O(22)	0.442 5(3)	0.032 3(2)	0.630 9(3)
O(23)	0.614 9(2)	0.085 0(2)	0.598 1(3)
O(24)	0.386 7(3)	0.204 7(3)	0.623 9(4)
C(11)	0.086 8(2)	0.065 2(3)	0.142 3(3)
C(12)	0.110 5(3)	−0.032 4(3)	0.156 0(4)
C(13)	0.208 8(3)	−0.059 2(2)	0.150 9(3)
C(14)	0.291 5(3)	0.269 1(3)	0.366 1(3)
C(15)	0.389 5(3)	0.242 4(3)	0.358 9(4)
C(16)	0.412 5(3)	0.145 0(2)	0.371 4(3)

isotropic and then with anisotropic thermal parameters. The Fourier map showed two malonate groups and two oxygen atoms about Cu(1) and four oxygen atoms about Cu(2). All sixteen hydrogen atoms in the asymmetric unit were located at stereochemically permissible positions from two successive difference electron density maps. Positional and isotropic thermal parameters of the hydrogen atoms were then allowed to refine along with all the parameters of non-hydrogen atoms. The final *R* value was 0.038, using 2030 observed reflections $[I > 2.5\sigma(I)]$; $R' = 0.040$, $w = 1.00[\sigma^2|F_o|^2 + 0.004|F_o|^2]$. The value of R' using all unique reflections is 0.057. Refinement was carried out using SHELX 76[17] and atomic scattering factors were taken from ref. 18.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 2 Bond distances (Å) and bond angles (°) for $[Cu(H_2O)_4][Cu\{CH_2(CO_2)_2\}_2(H_2O)_2]$ with e.s.d.s in parentheses

Cu(1)–O(11)	1.948(3)	Cu(2)–O(110)	2.393(4)
Cu(1)–O(12)	1.951(3)	Cu(2)–O(21)	1.928(3)
Cu(1)–O(13)	1.947(3)	Cu(2)–O(22)	1.921(3)
Cu(1)–O(14)	1.942(3)	Cu(2)–O(23)	1.934(3)
Cu(1)–O(15)	2.414(4)	Cu(2)–O(24)	1.920(4)
Cu(1)–O(16)	2.511(4)		
O(11)–C(16)	1.268(5)	O(19)–C(14)	1.238(5)
O(12)–C(14)	1.272(5)	O(110)–C(16)	1.254(5)
O(13)–C(11)	1.269(5)	C(11)–C(12)	1.514(6)
O(14)–C(13)	1.272(5)	C(12)–C(13)	1.516(6)
O(17)–C(11)	1.238(5)	C(14)–C(150)	1.513(6)
O(18)–C(13)	1.241(4)	C(15)–C(16)	1.507(5)
O(15)–Cu(1)–O(16)	178.9(1)	O(12)–Cu(1)–O(14)	179.3(1)
O(14)–Cu(1)–O(16)	89.3(1)	O(12)–Cu(1)–O(13)	89.1(1)
O(14)–Cu(1)–O(15)	91.2(1)	O(11)–Cu(1)–O(16)	90.1(1)
O(13)–Cu(1)–O(16)	89.3(1)	O(11)–Cu(1)–O(15)	89.0(1)
O(13)–Cu(1)–O(15)	91.6(1)	O(11)–Cu(1)–O(14)	88.5(1)
O(13)–Cu(1)–O(14)	91.5(1)	O(11)–Cu(1)–O(13)	179.4(1)
O(12)–Cu(1)–O(16)	90.7(1)	O(11)–Cu(1)–O(12)	90.8(1)
O(12)–Cu(1)–O(15)	88.9(1)	Cu(1)–O(13)–C(11)	126.2(3)
Cu(1)–O(11)–C(16)	126.0(2)	Cu(1)–O(14)–C(13)	125.6(3)
Cu(1)–O(12)–C(14)	125.2(3)	Cu(2)–O(110)–C(16)	120.8(2)
O(110)–Cu(2)–O(24)	95.7(2)	O(22)–Cu(2)–O(24)	89.9(2)
O(110)–Cu(2)–O(23)	89.2(1)	O(22)–Cu(2)–O(23)	89.4(1)
O(110)–Cu(2)–O(22)	91.3(1)	O(21)–Cu(2)–O(24)	90.5(2)
O(110)–Cu(2)–O(21)	95.3(1)	O(21)–Cu(2)–O(23)	89.5(1)
O(23)–Cu(2)–O(24)	175.1(2)	O(21)–Cu(2)–O(22)	173.3(2)
O(13)–C(11)–O(17)	122.3(4)	O(12)–C(14)–O(19)	122.2(4)
C(12)–C(11)–O(17)	117.6(3)	C(15)–C(14)–O(19)	117.0(4)
O(13)–C(11)–C(12)	119.9(3)	C(15)–C(14)–O(12)	120.8(4)
C(11)–C(12)–C(13)	118.4(3)	C(14)–C(15)–C(16)	117.9(4)
O(18)–C(13)–C(12)	117.7(3)	O(110)–C(16)–C(15)	117.8(4)
O(14)–C(13)–C(12)	120.3(3)	O(11)–C(16)–C(15)	120.7(4)
O(14)–C(13)–O(18)	122.0(4)	O(11)–C(16)–O(110)	121.5(3)

Results and Discussion

Description of the Crystal Structure.—The asymmetric unit consists of a linked diaquabis(malonato)cuprate(II) anion and a tetraaquacopper(II) cation. Fig. 1 shows the atom labelling scheme. Fractional atomic coordinates are listed in Table 1.

Atom Cu(1) adopts square-bipyramidal co-ordination. The co-ordination octahedron is formed by the four carboxylate groups from two malonate ions and two oxygen atoms from water molecules. The four coplanar carboxylate oxygens O(11), O(12), O(13) and O(14) co-ordinate with equal copper–oxygen bond lengths forming the corners of an almost perfect square; water-oxygen atoms O(15) and O(16) co-ordinate axially. The copper atom is raised by 0.057(6) Å above the square base in the direction of O(15). This displacement of the copper atom contributes to the difference in length of two axial bonds, Cu(1)–O(15) [2.414(4) Å] being shorter by 0.1 Å than Cu(1)–O(16) [2.511(4) Å]. The average value of the copper–oxygen bond lengths in the square plane [1.947(3) Å] lies well within the range for similar bonds with carboxylate (1.92–2.16 Å).[19] The difference (0.515 Å) in the average length of the axial bonds and the equatorial bonds is in excellent agreement with the value $R_L - R_S$ (0.51 Å), reported by Hathaway,[19] where R_L and R_S represent lengths of the axial and equatorial bonds between copper and oxygen. All the bond angles around Cu(1) are close to 90°. Table 2 lists the bond distances and bond angles.

The co-ordination about Cu(2) is square pyramidal. Four oxygen atoms, O(21), O(22), O(23) and O(24) from water molecules situated in the same plane, form the corners of an almost perfect square with nearly equal bond lengths. The cationic and anionic portions of the structure are linked by a strong co-ordinate bond to give, overall, a neutral binuclear entity with the keto oxygen atom, O(110), from one malonate ion [chelated to Cu(1)], being also co-ordinated axially to Cu(2) [Cu(2)–O(110) 2.393(4)] which is displaced by 0.0997(6) Å from

Table 3 Magnetic data, χ_M and μ_{eff}, for $[Cu(H_2O)_4][Cu\{CH_2(CO_2)_2\}_2(H_2O)_2]$

T/K	$10^6\ \chi_M$/cm^3 mol^{-1}	μ_{eff} per Cu
80	16 873	2.71
96	11 013	2.06
148	5 151	1.75
186	4 458	1.83
225	3 676	1.83
297	3 325	1.99

its square plane towards O(110). Similar displacement of copper towards the direction of axial co-ordination is quite common among structures containing five-co-ordinated copper.[19-22] The average length of the equatorial bonds [1.926(3) Å] with Cu(2) is slightly shorter than those in the anionic counterpart of the complex.

Each –C–C(O)=O group in the complex anion is itself planar; *trans* C–C(O)=O groups are coplanar with each other. The dihedral angle between the planes defined by O(14), C(13), O(18), C(12) and O(12), C(14), O(14), O(15) is 1.5(2)°; the angle between the mean planes calculated for the sets of atoms O(11), C(16), O(110), C(15) and O(13), C(11), O(17), C(12) is 2.5(1)°.

The crystal structure is stabilised through extensive hydrogen bonding involving the carboxyl groups and water molecules. All the hydrogen atoms capable of forming hydrogen bonds are involved in hydrogen bond formation with either a keto or a carboxylate oxygen co-ordinated to Cu(1). Each keto oxygen atom including O(110), which is bonded to Cu(2), participates in hydrogen bonding with two different water molecules; the carboxylate oxygen atoms participate in one hydrogen bond each. All these hydrogen bonds are fairly strong, the largest acceptor–hydrogen distance being 2.16(7) Å. In all the hydrogen bonds the water oxygens act as the donor atoms with the keto or carboxylate oxygens acting as acceptor atoms.

Infrared Spectra.—The IR spectrum of the copper(II) malonate shows a broad band at *ca.* 3440 cm^{-1} due to O–H vibrations of co-ordinated water. Two strong bands at 1640 and 1440 cm^{-1} may be assigned to ν_{asym} and ν_{sym} vibrations of monodentate carboxylate. A further band at 1560 cm^{-1} may be due to ν_{asym} of bridging carboxylate.

Electronic Spectra.—The electronic spectra of the copper(II) malonate as a Nujol mull exhibits a broad shoulder at *ca.* 700 nm, weak shoulders at 490 and 360 nm, and a peak at *ca.* 240 nm. Similar observations were made with a thin KBr pellet of the compound where the bands at 490 and 360 nm are more prominent. The band at 360 nm was previously considered[12,23-27] as characteristic of binuclear 'copper acetate type' carboxylate-bridged complexes, in which there is a strong magnetic interaction between the two copper(II) centres within a dimer. However, the presence of this band in the present complex, in which there is little interaction between the two carboxylate-bridged copper(II) units, suggests that a degree of caution needs to be exercised in interpreting this band, which requires a much more detailed theoretical analysis than has so far been undertaken.

In aqueous solution, however, the electronic spectrum changes appreciably. A very broad band at λ_{max} 770 nm is observed, as well as shoulders at 255, 227 and 200 nm. This large shift in spectral peak positions in the visible as well as UV region indicates that in aqueous solution the species present is quite different from that found in the solid state.

Magnetic Susceptibility and EPR Spectroscopy Studies.—The magnetic susceptibility of the copper(II) malonate was studied at six different temperatures, between 297 and 80 K. Table 3 lists the molar susceptibility values at different temperatures and the corresponding magnetic moments. More extensive data have been reported for a related species by Dubicki[12] and Figgis[13] and their respective co-workers. However, these measurements provided values ($\mu_{eff}^{r.t.} = 1.77$, $\theta = 10$ K;[12] $\mu_{eff}^{r.t.} = 1.86$, $\theta = -2$ K[13]) different from those obtained in our study. Additionally the electronic spectrum of the complex reported in ref. 12 differs (360 nm band absent) from ours.

We found that at higher temperature the molar susceptibility shows Curie-Weiss behaviour with a large negative value of θ (≈ 100 K). However at lower temperatures (96 and 80 K) the molar susceptibility deviates to a substantial extent from the straight-line plot typical of Curie-Weiss behaviour, the observed values being appreciably lower than that obtained from extrapolation of the above straight line plot. In the absence of additional data at lower temperatures, it would not be proper to make any definitive comment as to why such a deviation occurs, but it may be due to the presence of a feeble antiferromagnetic interaction ($J \ll kT$ at room temperature) between the two copper atoms of the dinuclear unit, whose effect is tangible only at low temperature when J becomes comparable with kT. The large (5.78 Å) copper–copper separation within the dinuclear unit suggests that if any exchange interaction at all takes place, it will be very weak indeed.

The powder EPR spectrum of the compound at room temperature exhibits a broad band which at liquid-nitrogen temperature resolves to two parallel lines ($g_\parallel$ 2.392, 2.394) and two perpendicular lines ($g_\perp$ 2.182, 2.146). The fact that two distinct resonances are observed for the two different copper moieties indicates that exchange interaction, if any, is very small indeed, as has been argued from susceptibility data. The axial spectrum with $g_\parallel > g_\perp > 2.04$ is consistent with tetragonally distorted octahedral or square-pyramidal structure around Cu^{II}.[28] However, the G values $[= (g_\parallel - 2)/(g_\perp - 2)]$ of 2.15 and 2.39 for the two coppers, both much less than the expected value ($\geqslant 4$),[28] indicates that some amount of exchange interaction is probably present. In aqueous solution at room temperature the compound showed a four-line EPR spectrum with $g_{iso} = 2.222$ and $A_{iso} = 52.5$ G (0.005 25 T), indicating that a single *mononuclear* species is present.

Conductance.—A conductivity study in aqueous solution shows that the copper(II) malonate is non-conducting with molar conductance $\Lambda_M = 15$ ohm^{-1} cm^2 mol^{-1}. If the binuclear species present in the solid state were also present in solution, it too would be non-conducting, however the electronic spectrum suggests that the species present in solution is quite different from that in the solid state. If the binuclear species present in the solid state were to break down to its constituent units, *i.e.* $[Cu(H_2O)_6]^{2+}$ and $[Cu\{CH_2(CO_2)_2\}_2(H_2O)_n]^{2-}$ (n = 1 or 2) ions then a conductance behaviour of a 2:1 electrolyte would have been expected. Moreover, in such a situation the observed electronic spectral changes upon dissolution would not be so dramatic. We propose that in aqueous solution the major species present is probably $[Cu\{CH_2(CO_2)_2\}(H_2O)_3]$ (although another distal co-ordinated water may be attached) as this can explain the experimentally observed solution conductance, EPR and electronic spectra. Our proposition is also supported by the stepwise formation constant data[29] which shows that the formation constant for a mono(malonato)copper(II) complex ($K_1 = 5.0 \times 10^5$ dm^3 mol^{-1}) is 1.58×10^3 times larger than that for addition of a second malonate leading to bis(malonato)copper(II) ($K_2 = 3.16 \times 10^2$ dm^3 mol^{-1}). The data clearly suggest in solution mono(malonato)copper(II) species will be present predominantly.

Exploration of Antitumour Activity.—The compound was tested for possible antitumour action using Leukemia screen 3PS 31 (host SCRO3 mice) and the results indicate that T/C (mean survival time of treated relative to control animal) is 130 at a dose level of 7.5 mg kg^{-1}. As this value is greater than

125, the compound exhibits significant antileukaemic activity against the above model and is worth further trial.

Conclusion

The present study demonstrates that in the solid state the bis(malonato) complex of copper(II) exists as a dinuclear unit containing a tetraaquacopper(II) cation and diaquabis(malonato)cuprate(II) anion linked through a novel type of carboxylate bridge. Our study also explains that because of the large Cu···Cu distance (5.78 Å) within the dinuclear unit there is very little magnetic interaction between them. The antileukaemic activity of the compound is also promising.

Acknowledgements

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References

1 *Magneto-structural Correlations in Exchange Coupled Systems*, eds. R. D. Willet, D. Gatteschi and O. Kahn, D. Reidel, Dordrecht, 1985.
2 J. Costes, F. Dahan and J. Laurent, *Inorg. Chem.*, 1992, **31**, 284 and refs. therein.
3 S. P. Perlepes, J. C. Huffman and G. Christou, *Polyhedron*, 1991, **10**, 2301.
4 I. Castro, J. Faus, M. Julve, F. Lloret, M. Verdaguer, O. Kahn, S. Jeannin, Y. Jeannin and J. Vaisserman, *J. Chem. Soc., Dalton Trans.*, 1990, 2207.
5 H. Okawa, N. Matsumoto, M. Koikawa, K. Takeda and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1990, 1383.
6 H. Okawa, M. Koikawa, S. Kida, D. Luneau and H. Oshio, *J. Chem. Soc., Dalton Trans.*, 1990, 469.
7 C. A. Salata, M. T. Youinou and C. J. Borrows, *Inorg. Chem.*, 1991, **30**, 3454.
8 F. Abraham, M. Lagrence, S. Sueur, B. Mernari and C. Bremard, *J. Chem. Soc., Dalton Trans.*, 1991, 1443.
9 M. Melink, M. D. Jurco and M. Handlovic, *Inorg. Chim. Acta*, 1984, **86**, 185.
10 *The Chemistry of Copper, Silver and Gold*, eds. A. G. Massey, N. R. Thompson, B. F. G. Johnson and R. Davis, Pergamon Texts in Inorganic Chemistry, vol. 17, Oxford, 1973.
11 O. Asai, M. Kishita and M. Kubo, *J. Phys. Chem.*, 1959, **63**, 96.
12 L. Dubicki, C. M. Harris, E. Kokot and R. L. Martin, *Inorg. Chem.*, 1966, **5**, 93.
13 B. N. Figgis and D. J. Martin, *Inorg. Chem.*, 1966, **5**, 100.
14 H. T. S. Britton and E. D. Jarrett, *J. Chem. Soc.*, 1935, 168.
15 S. E. Sherman and S. J. Lippard, *Chem. Rev.*, 1987, **87**, 1153.
16 A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, ELBS, London, 3rd edn., 1962, p. 497.
17 G. M. Sheldrick, SHELX 76, a Program for Crystal Structure Determination, Cambridge University, 1976.
18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
19 B. J. Hathaway, *Struct. Bonding (Berlin)*, 1973, **14**, 49.
20 H. C. Freeman, G. Robinson and J. C. Schoone, *Acta Crystallogr.*, 1964, **17**, 719.
21 B. Strandberg, I. Rindqvist and R. Rosenstein, *Z. Kristallogr.*, 1961, **116**, 266.
22 J. A. Goedkoop and C. H. MacGillavry, *Acta Crystallogr.*, 1957, **10**, 125.
23 R. Tsuchida, S. Yamada and H. Nakamura, *Nature (London)*, 1958, **181**, 2479.
24 S. F. A. Kettle and A. J. P. Pioli, *J. Chem. Soc. A*, 1968, 1243.
25 R. Tsuchida and S. Yamada, *Nature (London)*, 1955, **176**, 1171.
26 R. Tsuchida, S. Yamada and H. Nakamura, *Nature (London)*, 1956, **178**, 1192.
27 L. Dubicki and R. L. Martin, *Inorg. Chem.*, 1966, **5**, 2203.
28 B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, 1970, **5**, 1.
29 A. E. Martell and R. M. Smith, *Critical Stability Constants*, Plenum Press, New York, 1977, vol. 3, p. 98.

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