DALTON
FULL PAPER

Pseudo-oxocarbons: the first complex of the 3,4-bis(dicyanomethylene)-cyclobutane-1,2-dione dianion ($cdcb^{2-}$); crystal structure of $[\{Cu_2(cdcb)(MeCN)_2\}_n]$

Christophe Pena,[a] Anne Marie Galibert,[a] Brigitte Soula,[a] Paul-Louis Fabre,[a] Gérald Bernardinelli[b] and Paule Castan*[,a]

[a] *Laboratoire de Chimie Inorganique, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France*

[b] *Laboratoire de Cristallographie, 24 Quai E. Ansermet, CH-1211 Geneva 4, Switzerland*

Reaction of copper(II) ion with 3,4-bis(dicyanomethylene)cyclobutane-1,2-dione dianion ($cdcb^{2-}$) led to a copper(I) complex, $[\{Cu_2(cdcb)(MeCN)_2\}_n]$. The crystal structure of this first complex of cdcb has been determined; it consists of layers of $Cu_2(cdcb)(MeCN)_2$ units parallel to the *ab* planes. The redox system of this complex, investigated by electrochemistry and ESR spectroscopy, is formed by the dianion, the radical anion, the neutral species of cdcb and the Cu^I–Cu^{II} system.

Much work has been devoted during the past years to squarate (3,4-dihydrocyclobut-3-ene-1,2-dionate) co-ordination chemistry, and its co-ordination modes are well known: chelating, bis(chelating) and monodentate, bis(monodentate) or tetra(monodentate).[1] In recent years several species have been synthesized in which one or more of the carbonyl oxygen atoms have been partially or completely substituted by other atoms leading to the so-called pseudo-oxocarbons. They include nitrogen, sulfur and selenium.[2] Among these pseudo-oxocarbons our interest was focused on derivatives in which one or more of the oxygen atoms are replaced with dicyanomethylidene groups $=C(CN)_2$. These additions on the cyclic delocalized system of the squarate ion lead to an extension of the π delocalization. These compounds are deeply colored with color changes according to the oxidation state and they are regarded as cyanine dyes.

The charge-transfer salts of the π-donor tetrathiofulvalene (TTF) [2-(1,3-dithiol-2-ylidene)-1,3-dithiole] with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as the acceptor are the best known examples of organic solids with high electrical conductivity and magnetic properties (the 'organic metals').[3] Tetracyanoquinodimethane and its radical anion form salts with most metal ions[4] and Melby *et al.*[4a] have reported the preparation and conductivity properties of some transition-metal complexes. These compounds present conductivities of the order of 10^{-4}–10^{-5} Ω^{-1} cm^{-1}. High symmetry, small molecular size and molecular planarity are among the factors generally considered to favor conductivity.

The 3,4-bis(dicyanomethylene)cyclobutane-1,2-dione dianion ($cdcb^{2-}$) presents a formal analogy with the doubly reduced TCNQ and a similarity of structure with that involved in organic semiconductors. However, to our knowledge, no report concerning its metal complexes has been published so far. In the present work we report the synthesis, structural characterizations and redox properties of the first complex obtained with cdcb as ligand, $[\{Cu_2(cdcb)(MeCN)_2\}_n]$.

Results and Discussion

Crystal structure

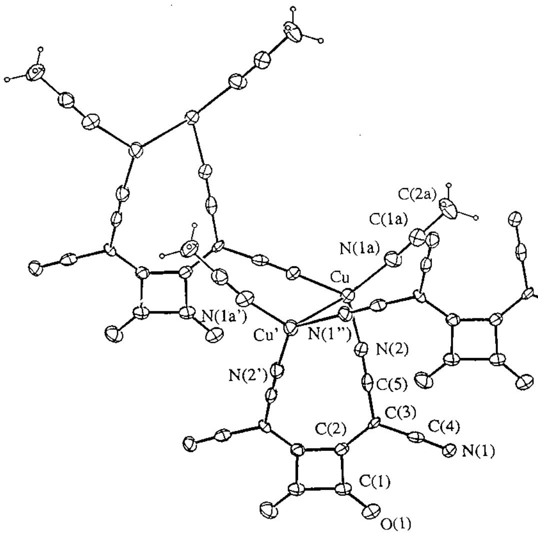
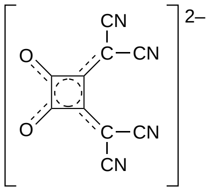


Fig. 1 Crystal structure of the complex $[Cu_2(cdcb)(MeCN)_2]$. Ellipsoids are at the 50% probability level



The dinuclear entity of the compound is shown in Fig. 1. The elementary unit presents a symmetry axis going over the middle of the Cu–Cu′ axis and the middle of the C(2)–C(2′) bond. In this complex the copper atom exhibits trigonal co-ordination: it is surrounded by three nitrogen atoms, two of them from the cyano groups of two different cdcb ions and the other from an acetonitrile molecule. Moreover, the symmetrically bonded Cu′ lies above this plane, and one copper environment may be described as a distorted trigonal pyramid with copper and three nitrogen atoms in the basal plane and another copper atom at the apical position. Thus the cdcb bridges two copper atoms of the same unit with a Cu ⋯ Cu distance of 3.1143(9) Å (Table 1) and two copper atoms of two different units with a Cu ⋯ Cu distance of 5.0218(8) Å corresponding to the symmetry operation $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$. It is clear that the distance between the two copper atoms is sufficiently great to preclude any significant metal–metal interaction in this dinuclear unit.

The square ring is planar (plane 1) and located on a two-fold

Table 1 Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

Metal environment			
Cu–Cu′ 3.1143(9)			
Cu–N(1)	1.904(4)	Cu–N(2)	1.903(3)
Cu–N(1a)	1.934(4)		
N(1)–Cu–N(2)	125.8(2)	N(1)–Cu–N(1a)	116.9(1)
N(2)–Cu–N(1a)	117.1(2)	N(1)–Cu–Cu′	66.2(1)
N(2)–Cu–Cu′	87.2(1)	N(1a)–Cu–Cu′	124.5(1)
Ligands			
C(1)–C(1′)	1.506(7)	C(1)–C(2)	1.483(5)
C(2)–C(2′)	1.416(7)	C(2)–C(3)	1.408(6)
C(3)–C(5)	1.422(5)	C(3)–C(4)	1.418(7)
C(1a)–C(2a)	1.452(7)	N(1a)–C(1a)	1.142(6)
Cu–N(1)–C(4)	178.7(3)	Cu–N(2)–C(5)	175.0(4)
Cu–N(1a)–C(1a)	170.3(3)		
O(1)–C(1)–C(2)	134.8(4)	O(1)–C(1)–C(1′)	136.9(3)
C(2)–C(1)–C(1′)	88.2(3)	C(1)–C(2)–C(3)	129.5(4)
C(1)–C(2)–C(2′)	91.7(3)	C(3)–C(2)–C(2′)	138.8(3)
C(2)–C(3)–C(4)	119.6(3)	C(2)–C(3)–C(5)	122.1(4)
C(4)–C(3)–C(5)	118.1(4)	N(2)–C(5)–C(3)	177.9(4)
N(1)–C(4)–C(3)	117.3(4)	N(1a)–C(1a)–C(2a)	178.8(5)

axis. This plane includes the atoms directly attached to it, O(1) and C(3), and the major deviations from the plane are +0.082 Å for O(1) and −0.092 Å for C(3). However, while the deviations of the cyano groups from the mean plane are very small in cdcb salts (sodium, rubidium and caesium),[5–7] the loss of planarity is important in the complex. The N(1), N(2), C(3), C(4) and C(5) atoms are coplanar (plane 2), the dihedral angle between the square ring plane and plane 2 being 15.96°. The angle between planes 2 and 3 [N(1′), N(2′), C(3′), C(4′) and C(5′)] is 31.28°. The dianion $cdcb^{2-}$ is a potential multidentate ligand: co-ordination may occur by the oxygen atoms, or more probably the nitrile groups, as a chelating ligand or through the four nitrogen atoms acting independently. In the present molecule it acts as a tetradentate ligand (the four nitrogen atoms being co-ordinated to four different metal atoms) (Fig. 2), and there is an opposite twist of the two $C(CN)_2$ groups in the structure. It may be underlined that the nitriles, which are chemically distinct when the ligand is planar, become more similar in this twisted form.

The C(2)–C(1) bond distance has a value of 1.483(5) Å, slightly longer than those observed in Rb_2(cdcb) [1.45(1) and 1.46(1) Å] and in Cs_2(cdcb) [1.46(1) Å]. In squaric acid the equivalent distances are 1.458(3) and 1.454(3) Å.[8] The C(1)–C(1′) distance of 1.506(7) Å is slightly longer than in alkali-metal salts, 1.475, 1.50(1) and 1.46(1) Å for sodium, rubidium and caesium respectively; the C–C distances are 1.47 Å in glyoxal and diacetyl.[9] There is little delocalization between the two carbonyl groups of the squarate ring. The C(2)–C(2′) bond distance [1.416(7) Å] is remarkably shorter than the other C–C bonds of the squarate ring, but also shorter than those observed in the alkali-metal salts. This value indicates a significant double-bond character while in squaric acid itself the double-bond distance is 1.405(3) Å.[8]

In our complex the $C_{ring}–C(CN)_2$ distance is 1.408(6) Å compared to 1.396(6) and 1.40(1) Å in the sodium and rubidium salts and to 1.374(3) Å in solid TCNQ.[10] The C(3)–C(4) and C(3)–C(5) distances corresponding to C–CN are 1.418(7) and 1.422(5) Å and are similar to those observed in $cdcb^{2-}$ salts. The C(4)–N(1) and C(5)–N(2) distances are 1.150(6) and 1.156(5) Å in this copper(I) complex [1.14(1) Å in the rubidium and caesium salts and 1.145(6) Å in the sodium salt], values which indicate that the C–N bond orders are not affected by complexation.

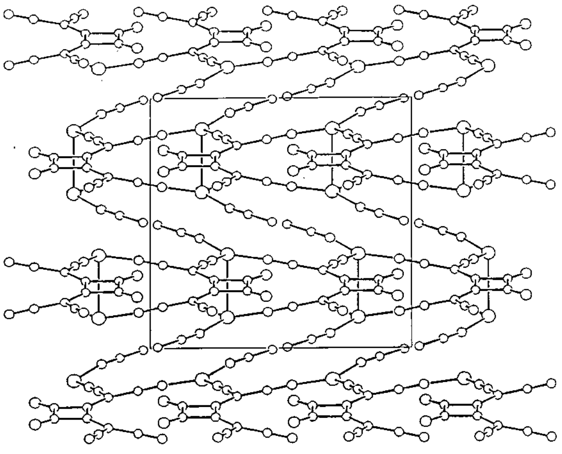


Fig. 2 Packing of the layers in $[\{Cu_2(cdcb)(MeCN)_2\}_n]$

The angles at atoms N(1a) and C(1a) [170.3(3) and 178.8(5)° respectively] show that the acetonitrile ligand is essentially linear and N-bound. The C–N bond distance (1.142 Å) is not distinguishable from the value determined for free MeCN (1.155 Å). This is consistent with co-ordinated acetonitrile acting as a simple σ-donor ligand without π-acceptor character.

Thus we conclude that the loss of planarity in the complex is accompanied by loss of the π delocalization of the ring, the π character being mainly spread out on the cyano side of the molecule.

Chemistry

A color change, pale green to emerald green, is observed when K_2(cdcb) is added to a copper(II) salt. The emerald green color is characteristic of a transient radical anion $cdcb^{\bullet -}$ associated with the reduction of Cu^{II} to Cu^{I}. The product obtained is diamagnetic, typical for a copper(I) complex, and an identical product is obtained by direct reaction of a copper(I) salt with K_2(cdcb).

IR spectra

The vibrational spectra of $cdcb^{2-}$ salts with alkali-metal cations have been analysed by Lunelli and co-workers.[11,12] The vibrational assignments were difficult due to the strong coupling of the two C=O oscillators and to C=O and C=C coupling. Bands near 2200 cm^{-1}, *i.e.* 2212, 2199 and 2190 cm^{-1}, for the potassium salt were assigned to ν(CN) stretching frequencies. For the copper complex these values are appreciably lower, at 2206, 2180 and 2155 cm^{-1}. These variations are attributed to co-ordination of the nitrile group to copper and also to the loss of ligand planarity when going from a salt to a co-ordinated nitrile. Moreover a band at 2222 cm^{-1} observed in the complex spectra is attributed to the ν(CN) of the linked acetonitrile. For free $cdcb^{2-}$ the bands at 1748 and 1627 cm^{-1} are attributed by Lunelli to the carbonyl group. For the complex one of these vibrations remains practically unchanged (1751 cm^{-1}), and so corresponds to a non-co-ordinated carbonyl stretching. However, the band at 1627 cm^{-1} for the ligand, which may be attributed to a carbonyl or a C=C stretching, is strongly shifted at 1712 cm^{-1}. We have attributed this vibration to a C=C bond, the shift being correlated to the localization of the C(2)–(C2′) double bond on going from the ligand to the complex.

Redox properties

As reported previously,[13] in acetonitrile, the voltammogram of $cdcb^{2-}$ at a platinum electrode presents two oxidation processes (Fig. 3), equations (1) and (2). The radical-anion is characterized by its ESR spectrum ($g = 2.004$).[10,14]

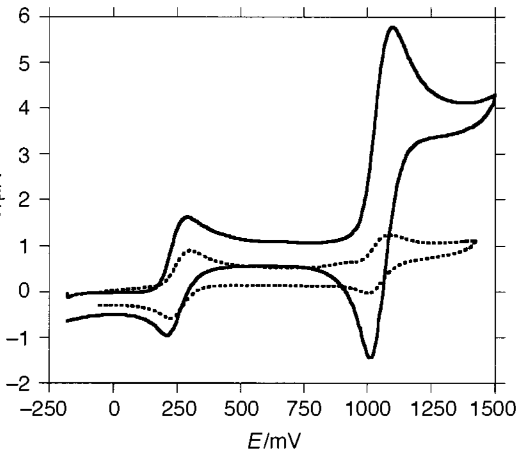


Fig. 3 Cyclic voltammogram in acetonitrile at a platinum disc electrode (diameter 1 mm, potential scan speed 0.1 V s^{-1}): ---, free $cdcb^{2-}$, 0.6 mmol dm^{-3}; —–, $[Cu_2(cdcb)(MeCN)_2]$, 1 mmol dm^{-3}

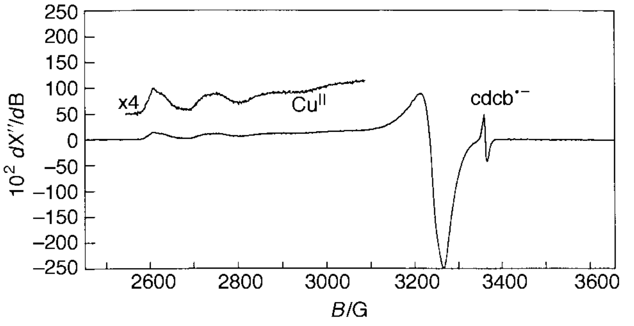


Fig. 4 X-Band ESR spectra of a frozen solution in acetonitrile of $[Cu_2(cdcb)(MeCN)_2]$: after partial electrolysis at 1.2 V, spectrum of the residual radical anion $cdcb^{\bullet-}$ and copper(II) complex. G = 10^{-4} T

$$\mathrm{cdcb}^{2-} \rightleftharpoons \mathrm{cdcb}^{\bullet-} + \mathrm{e} \qquad E_{\frac{1}{2}} = 0.243\ \mathrm{V} \tag{1}$$

$$\mathrm{cdcb}^{\bullet-} \rightleftharpoons \mathrm{cdcb} + \mathrm{e} \qquad E_{\frac{1}{2}} = 1.046\ \mathrm{V} \tag{2}$$

In the electroactivity domain of acetonitrile, the general cyclic voltammogram of $[\{Cu_2(cdcb)(MeCN)_2\}_n]$ shows different electrochemical systems: on the cathodic side, a reduction of Cu^I to metallic Cu (peak potential −0.5 V) (on the reverse scan a typical redissolution peak is observed for the copper reoxidation, peak potential −0.28 V); on the anodic side, two oxidation processes. The electrochemical study was restricted to the oxidation processes. These two processes appear reversible whatever the potential scan speed. By comparison with ferrocene, these electrochemical systems are classified as reversible with a high electron-transfer rate. The values of the peak potentials match those of the free $cdcb^{2-}$ oxidations. Furthermore, while the latter oxidation proceeds through two successive one-electron transfers, the oxidation of the complex first proceeds through a one-electron transfer followed by a three-electron transfer, equations (3) and (4).

$$[\mathrm{Cu_2(cdcb)}] \rightleftharpoons [\mathrm{Cu_2(cdcb^{\bullet})}]^{+} + \mathrm{e} \qquad E_{\frac{1}{2}} = 0.243\ \mathrm{V} \tag{3}$$

$$[\mathrm{Cu_2(cdcb^{\bullet})}]^{+} \rightleftharpoons [\mathrm{Cu_2(cdcb)}]^{4+} + 3\ \mathrm{e} \qquad E_{\frac{1}{2}} = 1.068\ \mathrm{V} \tag{4}$$

This electrochemical pathway was confirmed by exhaustive electrolysis monitored by ESR measurements. After exhaustive electrolysis of the complex at 0.6 V (on the plateau of the first wave, Fig. 3), the solution turned deep green and coulometric determinations showed a one-electron transfer. The ESR spectrum is characteristic of the organic radical $[Cu_2(cdcb^{\bullet})]^+$ ($g = 2.0038$). No free Cu^+/Cu^{2+} signal was detected by voltammetry, meaning that the radical anion is still a ligand. By continuation of the electrolysis at 1.2 V (on the plateau of the second wave) the solution turned light yellow. After an exchange of 1.8 e per ligand, the ESR spectrum (Fig. 4) shows the disappearance of the radical-anion $cdcb^{\bullet-}$ signal in $[Cu_2(cdcb^{\bullet})]^+$ and the appearance of a copper(II) signal ($g_{\perp} = 2.083$ and $g_{\parallel} = 2.39$). These electrolyses confirmed the oxidation of both Cu^I and $cdcb^{\bullet-}$. This is consistent with a compressed tetrahedral complex of Cu^{II} with two cdcb anions and two acetonitriles as ligands.[15] During the electrolysis an equilibrium exists between the two redox couples Cu^I–Cu^{II} and $cdcb^{\bullet-}$–cdcb in the complex and their electrochemical systems cannot be separated. A question remains as to the location of the electron transfer: on the ligand, on the copper centers or on both redox centers. In each case, intramolecular exchange induces the coexistence of Cu^{II} and radical anion.

Experimental

Reactants and methods

Squaric acid was obtained from Aldrich. All other chemicals and solvents were of reagent grade. The salt $K_2(cdcb)$ was prepared according to Sprenger and Ziegenbein.[5] Infrared spectra were recorded in the solid state as Nujol mulls on a Perkin-Elmer 983 G spectrometer.

Electrochemical measurements were carried out with a laboratory-made potentiostat controlled by a personal computer at room temperature. The electrochemical cell (10 cm^3) was a conventional one with three electrodes: working electrode, Pt (diameter 2 mm, EDI Tacussel) for rotating-disc electrode experiments and Pt (disc diameter 1 mm) for cyclic voltammetry experiments; counter electrode, platinum wire; and reference electrode, double junction saturated calomel electrode. The experiments were carried out in 0.1 mol dm^{-3} acetonitrile–NBu_4PF_6. Acetonitrile (Aldrich Gold label) and NBu_4PF_6 (Aldrich Electrochemical grade) were used without further purification. Electrolyses were conducted in the same electrochemical cell with the counter electrode separated from the solution by a fritted glass; they were monitored by ESR measurements on a 9 GHz Bruker (ESP 300 E) instrument.

Preparation of $[\{Cu_2(cdcb)(MeCN)_2\}_n]$

The compound was obtained by reaction of $K_2(cdcb)$ (0.286 g, 1 mmol) in water (100 cm^3) with $CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol) dissolved in water–acetonitrile 10:100 cm^3). From the first drops of $K_2(cdcb)$ added, the pale green solution became strongly green, then black. Suitable red-brown crystals (yield 80%) were obtained after standing the solution for 3 weeks under slow evaporation, at room temperature (Found: C, 39.78; H, 1.46; N, 19.91. Calc. for $C_{14}H_6Cu_2N_6O_2$: C, 40.20; H, 1.43; N, 20.14%).

Crystallography

A small crystal was mounted on a glass fiber with RS3000 oil. Crystal data, intensity measurements and structure refinement are summarized in Table 2. Graphite-monochromatized Cu-Kα radiation (λ 1.5418 Å) was employed as X-ray source. Unit-cell parameters and diffracted intensities were measured at 200 K with the scan mode ω–2θ on a STOE-STADI 4 diffractometer. The structure was solved by direct methods (MULTAN 87)[16] and refined by full-matrix least-squares with the XTAL 3.2 program.[17] Atomic scattering factors and anomalous dispersion terms were taken from ref. 18. All H atom co-ordinates were refined using fixed U_{iso} 0.05 $Å^2$.

CCDC reference number 186/787.

See http://www.rsc.org/suppdata/dt/1998/239/ for crystallographic files in .cif format.

Acknowledgements

We gratefully acknowledge Drs. D. de Montauzon and A. Mari,

Table 2 Summary of crystal data, intensity measurements and structure refinement

Empirical formula	$C_{14}H_6Cu_2N_6O_2$
Color	Red-brown
Crystal size/mm	0.06 × 0.189 × 0.30
M	208.7
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	10.6353(6)
b/Å	11.5204(8)
c/Å	12.7370(6)
β/°	110.946(3)
U/Å^3	1457.4(2)
Z	4
D_c/g cm^{-3}	1.90
F(000)	824
μ(Cu-Kα)/mm^{-1}	3.801
A^*_{min}, A^*_{max}	1.280, 2.367
hkl Ranges	−10 to 10, 0–11, 0–13
Scan range, 2θ/°	6–50
No. measured reflections	1690
No. independent reflections	845
No. observed reflections [$\lvert F_o \rvert \geq 4\sigma(F_o)$]	793
No. parameters	119
Weighting scheme, w	$1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\mathrm{max}}$	0.00053
Maximum, minimum ΔF/e Å^{-3}	0.53, −0.33
Goodness of fit S	3.84
R, R'	0.031, 0.024

Laboratoire de Chimie de Coordination, Toulouse, for technical assistance with electrochemical and ESR measurements.

References

1 G. Doyle, K. A. Eriksen, M. Modrick and G. Ansell, *Organometallics*, 1982, **12**, 1614; A. Weiss, E. Rigler, I. Alt, H. Böhme and C. Robl, *Z. Naturforsch.*, *Teil B*, 1986, **41**, 18; A. Weiss, E. Rigler and C. Robl, *Z. Naturforsch.*, *Teil B*, 1986, **41**, 1329; 1333; C. Robl and A. Weiss, *Z. Naturforsch.*, *Teil B*, 1986, **41**, 1341; R. Soules, F. Dahan, J. P. Laurent and P. Castan, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 587; G. Bernardinelli, D. Deguenon, R. Soules and P. Castan, *Can. J. Chem.*, 1989, **67**, 1158; O. M. Naghi, G. Li and T. L. Groy, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 727; X. Solans, M. Aguilo, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 775; J. C. Trombe, J. F. Petit and A. Gleizes, *New J. Chem.*, 1988, **12**, 197; *Inorg. Chim. Acta*, 1990, **167**, 69.

2 R. West, *Oxocarbons*, Academic Press, New York, 1980.

3 S. Kagoshima, *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum, New York, 1982 and refs. therein; H. Endres, *ibid.*, and refs. therein.

4 (*a*) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Moche, *J. Am. Chem. Soc.*, 1962, **84**, 3374; (*b*) A. R. Siedle, *J. Am. Chem. Soc.*, 1975, **97**, 5931; (*c*) P. Kathirgamanathan and D. R. Rosseinsky, *J. Chem. Soc.*, *Chem. Commun.*, 1980, 839.

5 H. E. Sprenger and W. Ziegenbein, *Angew. Chem.*, *Int. Ed. Engl.*, 1967, **6**, 553.

6 V. Busetti and B. Lunelli, *J. Phys. Chem.*, 1986, **90**, 2052.

7 B. Lunelli and V. Busetti, *J. Mol. Struct.*, 1987, **160**, 287.

8 Y. Wang, G. Stucky and J. M. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, 1974, 35.

9 J. E. Lu Valle and V. Schomaker, *J. Am. Chem. Soc.*, 1939, **61**, 3250.

10 R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Crystallogr.*, 1965, **18**, 932.

11 B. Lunelli and M. G. Giordini, *J. Mol. Struct.*, 1990, **218**, 303.

12 B. Lunelli, C. Corvaja and G. Farnia, *Trans. Faraday Soc.*, 1971, **67**, 1951.

13 L. M. Doane and A. J. Fatiadi, *Angew. Chem.*, 1982, **94**, 649; G. Capobianco, G. Farnia, G. Gennaro and B. Lunelli, *J. Electroanal. Chem. Interfacial Electrochem.*, 1982, **142**, 201.

14 (*a*) T. A. Blinka and R. West, *Tetrahedron Lett.*, 1983, **24**, 1567; (*b*) C. Corvaja, G. Farnia and B. Lunelli, *J. Chem. Soc.*, *Faraday Trans.*, 1975, 1293.

15 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 533 and refs. therein.

16 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, MULTAN 87, A system of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, Universities of York and Louvain-la-Neuve, 1987.

17 S. R. Hall and J. M. Steward (Editors), *XTAL 3.2 Users Manual*, Universities of Western Australia and Maryland, 1992.

18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 21*st July* 1997; *Paper* 7/05200F