

probably a result of steric interactions between the AF ligand and the macrocycle. Benzyl and azaferrocene ligands coordinated to the upper and lower site are centrosymmetrically located on each side of the macrocycle (Fig. 2), so that steric interactions between benzyl and one DH unit, and AF and the other one, could be equally spread.

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## Two Different (Croconato)(2,2':6',2''-terpyridyl)copper(II) Complexes in One Single Crystal: Structure of $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{H}_2\text{O})(\text{C}_5\text{O}_5)][\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{C}_5\text{O}_5)] \cdot 4\text{H}_2\text{O}$

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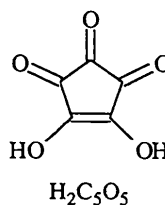
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**Abstract.**  $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{C}_5\text{O}_5)(\text{H}_2\text{O})][\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{C}_5\text{O}_5)] \cdot 4\text{H}_2\text{O}$ ,  $M_r = 963.8$ , triclinic,  $P\bar{1}$ ,  $a = 15.204$  (3),  $b = 12.825$  (2),  $c = 11.006$  (2) Å,  $\alpha = 84.18$  (2),  $\beta = 110.18$  (2),  $\gamma = 105.22$  (2)°,  $V = 1944$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.646$  Mg m<sup>-3</sup>,  $F(000) = 984$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 1.17$  mm<sup>-1</sup>,  $T = 288$  K, final  $R = 0.062$  and  $wR = 0.070$  for 3664 observed reflections. The crystal structure consists of two neutral mononuclear copper(II) entities of formula  $[\text{Cu}(\text{terpy})(\text{C}_5\text{O}_5)]$  (1) and  $[\text{Cu}(\text{terpy})(\text{C}_5\text{O}_5)(\text{H}_2\text{O})]$  (2) and four uncoordinated water molecules. The coordination of the copper(II) ion in (1) may be viewed as a square-based pyramid with the three N atoms of the 2,2':6',2''-terpyridine and an O atom of the croconate building the basal plane, whereas another O atom of the croconate

occupies the apical site. In (2), 2,2':6',2''-terpyridine and croconate act also as terdentate and bidentate ligands, respectively, but a water molecule occupies the sixth position leading to a distorted octahedral environment.

**Introduction.** The cyclic oxocarbon dianions,  $\text{C}_n\text{O}_n^{2-}$  (delatate, squarate, croconate and rhodizonate, for  $n = 3, 4, 5$  and 6, respectively) have been recognized as a family of unusually stable species with electron



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delocalization around the ring (West & Niu, 1969). Although oxocarbons have been known for more than 150 years, successful syntheses of deltic, squaric croconic (see scheme) and rhodizonic acids starting from di-*tert*-butoxyethyne have been achieved only very recently (Serratosa, 1983). X-ray diffraction studies of the anion salts indicate symmetric, planar structures for squarate (Macintyre & Werkema, 1964) and croconate (Baenziger & Hegenbarth, 1964). Owing to the simplicity and high degree of symmetry exhibited by these cyclic oxocarbons, their structures are especially suited for theoretical studies. Predictions about their aromatic character have been substantiated by theoretical calculations on delocalization energies and by the results of a study of their vibrational spectra (West & Powell, 1963; Ito & West, 1963; West, Eggerding, Perkins, Handy & Tuazon, 1979). However, the existence of aromaticity in these dianions is a subject of controversy (Aihara, 1981).

We are interested in the chelating properties of these multiatomic ligands as part of our programme on the synthesis and structural and magnetic properties of polynuclear complexes of Cu<sup>II</sup> bridged by extended ligands such as oxalate (Julve, Verdaguer, Gleizes, Philoche-Levisalles & Kahn, 1984), oxamide-oxamate (Verdaguer, Kahn, Julve & Gleizes, 1985) and 2,2'-bipyrimidine (Julve, De Munno, Bruno & Verdaguer, 1987).

The title compound was prepared as follows: an aqueous solution of sodium rhodizonate [Na<sub>2</sub>C<sub>6</sub>O<sub>6</sub>, (0.5 mmol)] was added to an acetonitrile solution of [Cu(terpy)](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (1 mmol). The resulting brown solution turned green after one day as originally observed by Gmelin (1825). Bulky dark green crystals were obtained by slow evaporation in the dark. Recrystallization from water yielded a green crystalline powder and dark green prismatic crystals of the title compound in low yield. In this, the starting rhodizonate anion has suffered an oxidative process involving ring contraction to yield the croconate anion. The structure of the title compound is of special significance because to our knowledge it is the first time that Gmelin's observation has been explained structurally.

**Experimental.** A crystal (0.1 × 0.1 × 0.15 mm) was mounted on a Philips PW 1100 four-circle diffractometer, equipped with a graphite monochromator and Mo K $\alpha$  radiation. The unit-cell parameters were determined from a least-squares fit of the angular settings of 25 reflections in the range  $4 \leq \theta \leq 12^\circ$ . The unit-cell parameters of the reduced cell are  $a = 11.006$  (2),  $b = 12.825$  (2),  $c = 15.204$  (3) Å,  $\alpha = 74.78$  (2),  $\beta = 69.82$  (2),  $\gamma = 84.18$  (2)°. The intensity data of 3792 reflections were measured in the range  $2 \leq \theta \leq 25^\circ$  ( $hkl$  range:  $-16$  to  $15$ ;  $0$  to  $15$ ;  $0$  to  $13$ ),

using the  $\omega$ -scan technique with scan width  $0.8^\circ$  and scan speed  $0.03^\circ \text{ s}^{-1}$ . 3664 were observed with  $I \geq 2.5\sigma(I)$ . Three reflections were measured every two hours as orientation and intensity controls; significant intensity decay was not observed. Lorentz-polarization, but not absorption corrections were made.

The structure was solved by direct methods, using *MULTAN84* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984) and refined by full-matrix least-squares method using *SHELX76* (Sheldrick, 1976). The function minimized was  $\sum w||F_o| - |F_c||^2$ , where the weighting scheme applied to each observation was  $w = (\sigma^2|F_o|^2 + 0.0048|F_o|^2)^{-1}$ . Non-water H atoms were assumed to be at the expected positions and refined with an overall isotropic temperature factor; the remaining atoms were refined anisotropically. The number of parameters refined was 658. The minimum and maximum heights in the final Fourier difference synthesis were  $0.4$  and  $-0.3 \text{ e } \text{Å}^{-3}$ , respectively, and the max.  $\Delta/\sigma$  was  $0.1$ . The final  $R$  and  $wR$  values were  $0.062$  and  $0.070$ , respectively, for all observed reflections. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final positional and equivalent isotropic temperature factors are given in Table 1,\* while selected bond distances and angles are listed in Table 2.

**Discussion.** The structure is made up of discrete molecules of [Cu(terpy)(C<sub>5</sub>O<sub>5</sub>)] (1) and [Cu(terpy)-(C<sub>5</sub>O<sub>5</sub>)(H<sub>2</sub>O)] (2) and four uncoordinated water molecules linked by van der Waals forces and hydrogen bonds (Table 2). The coexistence of two molecular complexes of Cu<sup>II</sup> bound to the same ligands is a quite unusual situation. As far as we know, for Cu<sup>II</sup> only a chlorocuprate(II) complex (Clay, Murray-Rust & Murray-Rust, 1973), two oxalato(bipyridyl)-copper(II) complexes (Julve, Faus, Verdaguer & Gleizes, 1984; Castro, Faus, Julve, Muñoz, Díaz & Solans, 1991) and an oxalato(terpyridyl)copper(II) complex (Castro, Faus, Julve & Gleizes, 1991) with such a property have been reported.

The Cu<sup>II</sup> ions display a square pyramidal [(1); Fig. 1] and a distorted octahedral coordination [(2); Fig. 2], respectively. Both complexes contain terdentate 2,2':6',2''-terpyridine and bidentate croconate ligands, the difference being a water molecule which occupies the sixth position in (2). The two N atoms of the terminal pair of pyridine rings in the terpy

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54773 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0502]

Table 1. Fractional coordinates ( $\times 10^4$ ,  $\times 10^5$  for Cu) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) of the non-H atoms with e.s.d.'s in parentheses
$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{\text{eq}}$
Cu(1)	1750 (8)	13700 (8)	28312 (11)	2.48 (5)
C(11)	482 (6)	3534 (7)	2413 (9)	2.26 (39)
O(11)	64 (5)	2797 (5)	3090 (6)	3.08 (31)
C(12)	1041 (6)	3282 (7)	1727 (9)	2.63 (40)
O(12)	1187 (5)	2361 (5)	1737 (6)	3.32 (32)
C(13)	1370 (7)	4268 (8)	1006 (10)	3.35 (47)
O(13)	1850 (6)	4386 (7)	316 (9)	5.71 (49)
C(14)	993 (7)	5133 (8)	1343 (10)	3.51 (48)
O(14)	1082 (6)	6059 (6)	921 (9)	5.56 (44)
C(15)	470 (7)	4663 (7)	2265 (11)	3.30 (46)
O(15)	87 (6)	5146 (6)	2790 (9)	5.74 (47)
N(101)	1036 (5)	1097 (6)	4624 (7)	2.60 (35)
C(102)	1436 (7)	1818 (8)	5596 (10)	3.37 (47)
C(103)	2070 (7)	1537 (9)	6818 (10)	3.96 (52)
C(104)	2227 (7)	520 (9)	7021 (10)	3.72 (50)
C(105)	1781 (7)	-223 (9)	6004 (10)	3.71 (51)
C(106)	1206 (7)	98 (7)	4822 (9)	2.79 (43)
C(107)	720 (7)	-598 (7)	3683 (9)	2.66 (42)
N(108)	157 (5)	-135 (6)	2680 (7)	2.51 (34)
C(109)	-384 (7)	-620 (7)	1574 (9)	2.47 (40)
C(110)	-387 (7)	-1661 (7)	1357 (10)	3.14 (46)
C(111)	200 (8)	-2192 (7)	2392 (11)	3.74 (52)
C(112)	750 (8)	-1654 (8)	3569 (11)	3.57 (51)
C(113)	-990 (6)	37 (7)	624 (9)	2.45 (39)
N(114)	-897 (5)	1021 (6)	1108 (7)	2.36 (32)
C(115)	-1423 (7)	1682 (7)	363 (9)	3.05 (44)
C(116)	-2057 (8)	1400 (8)	-873 (10)	3.82 (50)
C(117)	-2140 (7)	426 (9)	-1347 (10)	3.63 (49)
C(118)	-1597 (7)	-263 (8)	-610 (9)	2.91 (43)
O(w1)	-1533 (7)	3192 (8)	3646 (10)	7.79 (64)
O(w3)	3264 (7)	7868 (8)	8024 (10)	7.13 (57)
O(w5)	1621 (16)	4397 (18)	7165 (22)	8.89 (152)
Cu(2)	45431 (8)	68111 (8)	21538 (11)	2.57 (5)
C(21)	5098 (7)	8863 (7)	3028 (9)	2.45 (41)
O(21)	4460 (5)	8319 (5)	2086 (6)	2.96 (29)
C(22)	5800 (7)	8397 (7)	4062 (9)	2.85 (44)
O(22)	5850 (5)	7466 (5)	4081 (6)	3.13 (31)
C(23)	6409 (8)	9247 (9)	5056 (11)	3.86 (54)
O(23)	7022 (6)	9101 (7)	6063 (8)	6.03 (48)
C(24)	6122 (9)	10265 (9)	4472 (13)	4.64 (61)
O(24)	6527 (7)	11191 (7)	4957 (10)	7.66 (58)
C(25)	5318 (8)	10024 (8)	3212 (11)	3.82 (53)
O(25)	4931 (7)	10681 (7)	2489 (10)	6.99 (54)
N(201)	3697 (6)	6125 (6)	3247 (7)	2.66 (34)
C(202)	3197 (7)	6593 (7)	3701 (9)	2.94 (43)
C(203)	2641 (8)	6044 (9)	4457 (10)	3.94 (53)
C(204)	2648 (7)	4991 (9)	4789 (10)	3.87 (51)
C(205)	3209 (7)	4473 (8)	4368 (9)	3.05 (44)
C(206)	3720 (7)	5069 (7)	3587 (9)	2.71 (41)
C(207)	4349 (7)	4653 (7)	3117 (8)	2.56 (40)
N(208)	4786 (5)	5396 (6)	2396 (7)	2.50 (33)
C(209)	5425 (7)	5164 (7)	1930 (8)	2.61 (40)
C(210)	5679 (8)	4198 (7)	2178 (10)	3.33 (46)
C(211)	5199 (8)	3449 (9)	2879 (10)	4.11 (54)
C(212)	4519 (8)	3625 (7)	3381 (9)	3.28 (47)
C(213)	5801 (6)	6093 (7)	1189 (8)	2.48 (39)
N(214)	5425 (5)	6949 (5)	1115 (7)	2.32 (32)
C(215)	5695 (7)	7818 (8)	397 (10)	3.42 (48)
C(216)	6350 (7)	7861 (8)	-255 (10)	3.48 (48)
C(217)	6763 (8)	7001 (9)	-162 (11)	3.89 (52)
C(218)	6472 (7)	6085 (8)	571 (10)	3.27 (46)
O(w2)	3177 (5)	6447 (6)	175 (7)	4.82 (38)
O(w4)	3952 (7)	9575 (7)	9711 (8)	6.26 (49)

Table 2. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with e.s.d.'s in parentheses

Molecule (1)		Molecule (2)	
Cu(1)—O(11)	1.940 (7)	Cu(2)—O(21)	1.962 (7)
Cu(1)—O(12)	2.318 (7)	Cu(2)—O(22)	2.393 (6)
Cu(1)—N(101)	2.012 (7)	Cu(2)—N(201)	2.033 (9)
Cu(1)—N(108)	1.946 (8)	Cu(2)—N(208)	1.920 (8)
Cu(1)—N(114)	2.028 (6)	Cu(2)—N(214)	2.007 (9)
O(11)—C(11)	1.311 (11)	Cu(2)—O(w2)	2.420 (7)
C(12)—C(11)	1.427 (16)	O(21)—C(21)	1.265 (9)
C(15)—C(11)	1.445 (16)	C(22)—C(21)	1.467 (13)
O(12)—C(12)	1.255 (12)	C(25)—C(21)	1.457 (13)
C(13)—C(12)	1.489 (13)	O(22)—C(22)	1.214 (12)
O(13)—C(13)	1.197 (17)	C(23)—C(22)	1.502 (13)
C(14)—C(13)	1.505 (17)	O(23)—C(23)	1.212 (13)
O(14)—C(14)	1.222 (12)	C(24)—C(23)	1.498 (17)
C(15)—C(14)	1.485 (17)	O(24)—C(24)	1.262 (14)
O(15)—C(15)	1.246 (17)	C(25)—C(24)	1.493 (15)
O(12)—Cu(1)—O(11)	81.9 (3)	O(22)—Cu(2)—O(21)	80.4 (2)
N(101)—Cu(1)—O(11)	98.9 (3)	N(201)—Cu(2)—O(21)	100.7 (3)
N(101)—Cu(1)—O(12)	106.3 (3)	N(201)—Cu(2)—O(22)	89.6 (3)
N(108)—Cu(1)—O(11)	172.4 (4)	N(208)—Cu(2)—O(1)	172.4 (2)
N(108)—Cu(1)—O(12)	105.6 (3)	N(208)—Cu(2)—O(22)	92.2 (2)
N(108)—Cu(1)—N(101)	79.9 (3)	N(208)—Cu(2)—N(201)	80.6 (4)
N(114)—Cu(1)—O(11)	99.3 (3)	N(214)—Cu(2)—O(21)	99.6 (3)
N(114)—Cu(1)—O(12)	89.1 (3)	N(214)—Cu(2)—O(22)	93.1 (3)
N(114)—Cu(1)—C(101)	157.6 (3)	N(214)—Cu(2)—N(201)	159.7 (3)
N(114)—Cu(1)—N(108)	80.3 (3)	N(214)—Cu(2)—N(208)	79.1 (3)
C(12)—C(11)—O(11)	121.5 (9)	O(w2)—Cu(2)—O(21)	90.1 (3)
C(15)—C(11)—O(11)	127.3 (10)	O(w2)—Cu(2)—O(22)	170.5 (3)
C(15)—C(11)—C(12)	111.2 (9)	O(w2)—Cu(2)—N(201)	91.7 (3)
C(11)—O(11)—Cu(1)	111.4 (7)	O(w2)—Cu(2)—N(208)	97.3 (3)
O(12)—C(12)—C(11)	123.5 (9)	O(w2)—Cu(2)—N(214)	89.0 (3)
C(13)—C(12)—C(11)	108.4 (9)	C(22)—C(21)—O(21)	122.9 (8)
C(13)—C(12)—O(12)	128.1 (11)	C(25)—C(21)—O(21)	127.3 (8)
O(12)—O(12)—Cu(1)	100.7 (7)	C(25)—C(21)—C(22)	109.5 (7)
O(13)—C(13)—C(12)	128.9 (11)	C(21)—O(21)—Cu(2)	112.5 (6)
C(14)—C(13)—C(12)	105.6 (10)	O(22)—C(22)—C(21)	123.7 (8)
C(14)—C(13)—O(13)	125.5 (9)	C(23)—C(22)—C(21)	108.9 (8)
O(14)—C(14)—C(13)	126.4 (12)	C(23)—C(22)—O(22)	127.4 (8)
C(15)—C(14)—C(13)	108.2 (8)	C(22)—O(22)—Cu(2)	100.5 (5)
C(15)—C(14)—O(14)	125.4 (12)	O(23)—C(23)—C(22)	125.0 (11)
C(14)—C(15)—C(11)	106.4 (10)	C(24)—C(23)—C(22)	104.6 (8)
O(15)—C(15)—C(11)	127.0 (10)	C(24)—C(23)—O(23)	130.2 (10)
O(15)—C(15)—C(14)	126.6 (9)	O(24)—C(24)—C(23)	124.6 (10)
		C(25)—C(24)—C(23)	109.9 (9)
		C(25)—C(24)—O(24)	125.4 (10)
		C(24)—C(25)—C(21)	106.5 (9)
		O(25)—C(25)—C(21)	127.5 (9)
		O(25)—C(25)—C(24)	126.1 (9)

Symmetry code: (i)  $-x, 1-y, 1-z$ ; (ii)  $x, y, z$ ; (iii)  $x, y, z-1$ ; (iv)  $1-x, 2-y, 1-z$ ; (v)  $1-x, 2-y, 2-z$ .

at a significantly shorter distance [average value: 1.933 (13)  $\text{\AA}$ ] as a result of the constrained ligand geometry. This pattern of the two outer Cu—N bonds being longer than the middle metal—N bond has also been observed in the reported structures of other [Cu(terpy)]<sup>2+</sup> complexes (Anderson, Packard & Wicholas, 1976; Arriortúa, Rojo, Amigó, Germain & Declercq, 1982; Rojo, Vlasse & Beltrán-Porter, 1983; Henke, Kremer & Reinen, 1983; Savariault,

ligand form bonds of nearly equal length to the metal ion [average value: 2.020 (10)  $\text{\AA}$ ]. The N atom of the central pyridine ring is bonded to the Cu<sup>II</sup> ion

Rojo, Arriortúa & Galy, 1983; Allman, Kremer & Kucharzcyk, 1984; Folgado, Ibáñez, Coronado, Beltrán, Savariault & Galy, 1988; Folgado, Coronado, Beltrán-Porter, Rojo & Fuertes, 1989; Solans, Aguiló, Gleizes, Faus, Julve & Verdaguer, 1990; Folgado, Gómez-Romero, Sapiña & Beltrán-Porter, 1990; Castro, Faus, Julve & Gleizes, 1991).

The largest deviations from the best-plane calculations through N(101), N(108), N(114) and O(11) in (1) and N(201), N(208), N(214) and O(21) in (2) are 0.04 (1) Å for N(108) and 0.08 (1) Å for N(208). These four atoms lie at the corners of a distorted square plane surrounding the metal ion. The main element of the distortion is the displacement of the metal ion from this mean basal plane toward the apical O(12) [0.166 (1) Å] and O(22) [0.186 (1) Å]. This out-of-plane displacement of the Cu<sup>II</sup> ion and the constrained geometry of the terpy ligand are

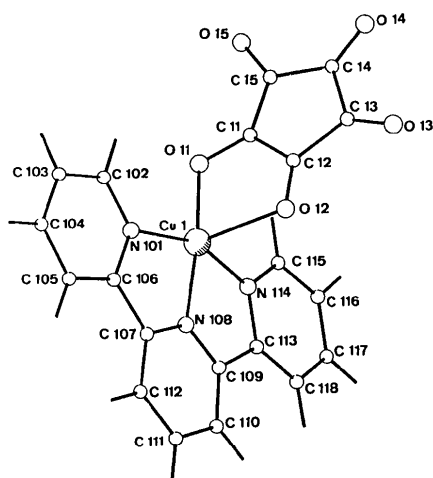


Fig. 1. Perspective view of molecule (1) showing the atom labelling.

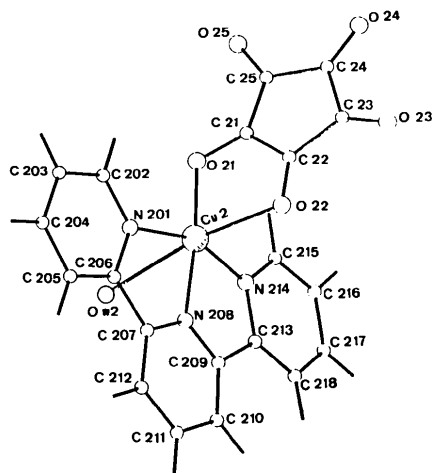


Fig. 2. Perspective view of molecule (2) showing the atom labelling.

evidenced by the values of the angles in the square-basal plane: whereas the N(101)—Cu(1)—N(108) and N(108)—Cu(1)—N(114) angles are significantly smaller than 90° [average value: 80.1 (2)°], the N(101)—Cu(1)—O(11) and N(114)—Cu(1)—O(11) angles are greater than 90° [average value: 99.1 (2)°]. Marked distortions of the angles involving *trans* ligands are also observed [157.6 (3) and 172.4 (4)° for N(101)—Cu(1)—N(114) and N(108)—Cu(1)—O(11), respectively]. These structural features are also observed in complex (2).

The croconate anion acts as a bidentate ligand in both complexes, being linked to the Cu<sup>II</sup> ion in an asymmetrical fashion. For Cu<sup>II</sup> this chelating behaviour of C<sub>5</sub>O<sub>5</sub><sup>2-</sup> is already known (Glick, Downs & Dahl, 1964). The Cu—O bond length *trans* to N is shorter [1.940 (7) and 1.962 (7) Å for Cu(1)—O(11) and Cu(2)—O(21), respectively] than the apical one [2.318 (7) and 2.393 (6) Å for Cu(1)—O(12) and Cu(2)—O(22), respectively]. The apical Cu—O(croconate) bond distance in the six-coordinated complex is longer than in the five-coordinated one due to the presence of a coordinated water molecule at 2.420 (7) Å in the former. In this complex the O(w2)—Cu(2)—O(22) angle is only 170.5 (3)°. The croconate ring is quite planar [largest deviations from the mean plane are 0.07 (1) Å for O(15) and -0.14 (1) Å for O(22)], and the dihedral angle between the terpy and C<sub>5</sub>O<sub>5</sub><sup>2-</sup> mean planes is 71.8 (5)° in (1) and 92.2 (5)° in (2).

The average C—C and C—O bond distances of the C<sub>5</sub>O<sub>5</sub><sup>2-</sup> ligand are close to the corresponding average values found for the croconate dianion with *D*<sub>5h</sub> symmetry in the diammonium salt, (NH<sub>4</sub>)<sub>2</sub>C<sub>5</sub>O<sub>5</sub> (Baenziger & Hegenbarth, 1964). However, a lengthening of C—O bond distances of the C<sub>5</sub>O<sub>5</sub><sup>2-</sup> ligand is observed for O coordinated to the metal ion [average values 1.28 (1) and 1.24 (1) Å for (1) and (2), respectively] with respect to the C—O bond distances in the diammonium salt [average value 1.21 (1) Å].

The shortest intermolecular copper—copper separations are 5.726 (1) and 8.126 (1) Å for Cu(1)⋯Cu(1)<sup>vi</sup> and Cu(1)⋯Cu(2)<sup>vii</sup>, respectively [symmetry code: (vi) -x, y, 1-z; (vii) -x, -y, -z].

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## Structures of Pd[(PPh<sub>2</sub>)<sub>2</sub>(NMe)]Cl<sub>2</sub>, Pt[(PPh<sub>2</sub>)<sub>2</sub>(NMe)]Cl<sub>2</sub> and Pt[(PPh<sub>2</sub>)<sub>2</sub>(NMe)](CN)<sub>2</sub>

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**Abstract.** [Bis(diphenylphosphino)methylamine]dichloropalladium (1), C<sub>25</sub>H<sub>23</sub>Cl<sub>2</sub>P<sub>2</sub>PdN, *M<sub>r</sub>* = 576.7, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 9.202 (1), *b* = 13.814 (1), *c* = 19.420 (1) Å, β = 92.45 (3)°, *V* = 2466 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.54 g cm<sup>-3</sup>, graphite-monochromatized Mo *Kα* radiation, λ = 0.71073 Å, μ = 10.9 cm<sup>-1</sup>, *F*(000) = 1160, room temperature, *R* = 0.039 for 3345 observed reflections [*I* > 3σ(*I*)]. [Bis(diphenylphosphino)methylamine]dichloroplatinum (2), C<sub>25</sub>H<sub>23</sub>Cl<sub>2</sub>P<sub>2</sub>PtN, *M<sub>r</sub>* = 665.41, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 9.246 (2), *b* = 13.916 (4), *c* = 19.333 (5) Å, β = 92.65 (2)°, *V* = 2485 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.78 g cm<sup>-3</sup>, graphite-monochromatized Mo *Kα* radiation, λ = 0.71073 Å, μ = 60.62 cm<sup>-1</sup>, *F*(000) = 1288, room temperature, *R* = 0.048 for 2329 observed reflections.

[Bis(diphenylphosphino)methylamine]dicyanoplatinum (3), C<sub>27</sub>H<sub>23</sub>P<sub>2</sub>PtN<sub>3</sub>, *M<sub>r</sub>* = 646.56, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 9.506 (3), *b* = 13.635 (5), *c* = 19.669 (7) Å, β = 93.32 (3)°, *V* = 2545 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.69 g cm<sup>-3</sup>, graphite-monochromatized Mo *Kα* radiation, λ = 0.71073 Å, μ = 57.1 cm<sup>-1</sup>, *F*(000) = 1256, room temperature, *R* = 0.041 for 3798 observed reflections. Three crystal structures of the bis(diphenylphosphino)methylamine (dppma) ligand chelating to a Pt-group metal atom are reported. The complexes (1) and (2) have chloride ligands *trans* to the dppma ligand while the third complex, (3), has cyanide ligands *trans* to the dppma ligand. The complexes have a highly distorted, square-planar coordination geometry. The ring strain associated with the four-membered chelate rings is evident in the distorted tetrahedral angles at P, which range from 93.3 (2) to 122.2 (5)°, and the

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