

**Discussion.** Final positional and thermal parameters are given in Table 1.\* Molecular geometry data are collected in Table 2. Fig. 1 shows the nickel coordination and the atomic numbering scheme. The complex molecules are centrosymmetrical. The nickel atoms lie on symmetry centers, and the oxygen, O(2), of a water molecule, on a mirror plane. The central nickel is pseudo-octahedrally coordinated by two *meso*-stien ligands and two acetates. The Ni—N distances (Table 2) are the usual distances found in pseudo-octahedral coordination, similar to 2.080 (4), 2.063 (5) and 2.103 (4) Å, found for bis(2-methyl-1,2-propanediamine)bis(trichloroacetato)nickel(II) (García-Granda & Gómez-Beltrán, 1984a). The N(1)—Ni—N(2) bite angle, 79.8 (1)°, and the N(1)—Ni—O(3) and N(2)—Ni—O(3) angles of 91.6 (1) and 91.0 (1)° are very close to the respective values of 82.5 (2), 91.1 (2) and 84.7 (2)° found in the cited compound. The angle between the plane through N(1)—Ni—N(2), and Ni(1)—O(3), is 88.3 (2)°. The octahedral coordination of this complex confirms the lack of steric hindrance expected from the structure of bis(*meso*-1,2-diphenyl-1,2-ethanediamine)nickel(II) dichloride dihydrate

\* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, hydrogen-bond distances and angles, least-squares-planes data and principal torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52332 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(García-Granda & Gómez-Beltrán, 1984b). Both molecules show a similar disposition of the *meso*-stien ligands, the torsion angle C(11)—C(1)—C(2)—C(21) being 51.1 (6)° in the present compound and 55.6 (6)° in the square-planar complex. The Ni—N distances are sensibly longer in an octahedral coordination than in the square-planar complex [1.922 (4) Å]. Water molecules contribute to the molecular packing through hydrogen bridges. There is also one intramolecular hydrogen bond connecting N(2) with the free oxygen of the acetate group O(4).

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## Structure and Single-Crystal Conductivity Measurements of Oxidized 3d Metal Phthalocyanines. Bis-Chloro Derivatives of Chromium(III), Iron(III) and Cobalt(III)

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**Abstract.** Dichloro(phthalocyaninato)iron(III), [Fe(C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>)Cl<sub>2</sub>], *M<sub>r</sub>* = 639.7, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 9.023 (2), *b* = 14.588 (2), *c* = 10.216 (5) Å, *β* =

97.58 (1)°, *V* = 1333.2 (7) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.57, *D<sub>x</sub>* = 1.592 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, *μ* = 0.805 mm<sup>-1</sup>, *F*(000) = 648, *T* = 298 K, *R* = 0.036, *wR* = 0.044 for 1510 reflections. Dichloro(phthalocyaninato)chromium(III), [Cr(C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>)Cl<sub>2</sub>], *M<sub>r</sub>* =

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636-9, monoclinic,  $P2_1/n$ ,  $a = 9.137$  (3),  $b = 14.734$  (2),  $c = 10.364$  (2) Å,  $\beta = 97.36$  (1)°,  $V = 1383.8$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.51$ ,  $D_x = 1.525$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.635$  mm<sup>-1</sup>,  $F(000) = 644$ ,  $T = 298$  K,  $R = 0.048$ ,  $wR = 0.091$  for 1162 reflections. Dichloro(phthalocyaninato)cobalt(III), [Co(C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>)Cl<sub>2</sub>],  $M_r = 642.7$ , monoclinic,  $P2_1/n$ ,  $a = 9.060$  (5),  $b = 14.640$  (2),  $c = 10.268$  (5) Å,  $\beta = 97.73$  (1)°,  $V = 1349.8$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.57$ ,  $D_x = 1.579$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.870$  mm<sup>-1</sup>,  $F(000) = 650$ ,  $T = 298$  K,  $R = 0.031$ ,  $wR = 0.037$  for 1225 reflections. Single crystals grown by electrochemical oxidation were studied by X-ray crystallography. The monoclinic solids are isostructural, and are characterized by four probe resistivity measurements as molecular semiconductors [ $10^{-2} < \sigma_{300\text{K}} < 10^{-3} \Omega^{-1} \text{cm}^{-1}$ ;  $E_a = 0.13$  (5) eV]. The molecular geometry and electrical conduction are discussed on an  $M^{\text{III}}$ -phthalocyanine-cation-radical structural model.

**Introduction.** According to the nature of the metal in metallophthalocyanines;  $MPc$  (with  $Pc = C_{32}H_{16}N_8^{2-}$ ), chemical oxidation is reported to affect  $M$ ,  $Pc$  or both (Myers, Rayner Canham & Lever, 1975; Mossoyan-Deneux, Benlian, Pierrot, Fournel & Sorbier, 1985) and will result in variations in geometry and electronic configuration. This behavior in the series is not always parallel to that of the homologous porphyrins (Kadish, Lin & Han, 1987) on which recent results have been published. Long after the first extensive report on their characterization (Myers, Rayner Canham & Lever, 1975), oxidized  $MPc$ 's raise a renewed interest, and data from spectral (Homborg & Kaltz, 1984; Kaltz & Homborg, 1983) or magnetic studies (Kadish, Lin & Han, 1987; Gans, Buisson, Duée, Marchon, Erler, Scholz & Reed, 1986; Groves, Takahashi & Butler, 1983) have been published on these complexes with a cationic radical ligand [labeled  $Pc^{+\cdot}$  or  $Pc(1-)$  by most authors]. Such structures play an active role in processes such as photoassisted catalysis (Loutfy & McIntyre, 1982) and electronic conduction (Meier, Albercht, Wöhrle & Jahn, 1986).

While several reports exist on the structure of chemically doped and mixed valence type solids obtained from  $MPc$ , no structure has been published on integral oxidation number complexes of general formula  $MPcCl_2$ . This is of particular importance since inserted anions or neutral molecules would have a great influence on the conductivity. The published papers report on solutions, powdered material or thin layer deposits obtained by the action of various oxidizing agents.

Among the numerous and extensive studies on doped  $MPcX$  conductors (Almeida, Kanatzidis, Tonge, Marks, Marcy, McCarthy & Kannewurf,

1987; Datz, Metz, Schneider & Hannack, 1984) with a non-integral oxidation number, and/or with a stacked or bridged polymeric structure, the only relevant studies are on  $NiPcX$  (Martinsen, Greene, Palmer & Hoffman, 1983; Palmer, Stanton, Hoffman & Ibers, 1986),  $FePcI$  (Palmer, Stanton, Jaggi, Hoffman, Ibers & Schwartz, 1985),  $CoPcI$  (Martinsen, Stanton, Greene, Tanaka, Hoffman & Ibers, 1985) and  $CrPcFI_{0.5}$  (mentioned along with  $GaPcF$ ) (Wynne & Nohr, 1982).

The present article describes the crystallographic results from well formed single crystals obtained by an electrochemical growth technique already described (Mossoyan-Deneux, Benlian, Pierrot, Fournel & Sorbier, 1985) for the case of  $ZnPc$ , which was the first non-doped crystalline semiconductor derived from  $MPc$  and obtained by anodic oxidation of an organic solution.

**Experimental.**  $CoPc$  and  $CrPc$  were prepared as usual from the metal salt and phthalonitrile (Barrett, Dent & Linstead, 1936).  $FePc$  in good yield and purity was obtained by an adapted procedure already described (Ouedraogo, Mossoyan-Deneux & Benlian, 1978). Sublimation in vacuum gave the starting material in suitable purity except for  $CrPc$  which includes detectable amounts of  $CrPcOH$  (Ercolani, 1966; Ercolani, Neri & Porta, 1967) which did not interfere in the subsequent reactions.  $FePc$  was converted into  $FePcCl$  by the method described by Barrett, Frey & Linstead (1938); this intermediate step was unnecessary in the case of  $CoPc$  which is stable enough in DMF. Once the solution was prepared in a controlled atmosphere with the suitable amount of solvent and carrier electrolyte, it was checked by voltammetry (differential pulse and cyclic) to define the best range of potential to perform each particular electrolysis. The protected cell was then connected to a PAR 173-276 Galvanostat monitored by an Apple IIe microcomputer. After 50 to 300 h of growth, black shiny crystals were collected, sparingly washed and selected for analysis, the larger ones being kept for X-ray and electrical measurements.

The samples are remarkably stable (identical electrical performance after several months in dry air at room temperature).

Medium sized crystals of  $FePcCl_2$  ( $0.3 \times 0.3 \times 0.4$  mm),  $CrPcCl_2$  ( $0.3 \times 0.3 \times 0.2$  mm) and  $CoPcCl_2$  ( $0.2 \times 0.2 \times 0.3$  mm) were selected for data collection,  $D_m$  by flotation in  $CCl_4$ -benzene mixture of known density, Enraf-Nonius CAD-4 diffractometer,  $Mo K\alpha$  radiation, cell constants were determined by least-squares procedure for 25 reflections ( $14 < \theta < 16^\circ$ ). Intensity data by  $\omega$ - $2\theta$  scan of  $0.91$ - $10.06^\circ \text{min}^{-1}$  over  $(1.0 + 0.35 \tan \theta)^\circ$ . For  $FePcCl_2$ ,  $\theta_{\text{max}} = 25^\circ$ , 2951 measured reflections, 2309 independent reflections in the range  $-7 < h < 7$ ,

$-12 < k < 12$ ,  $0 < l < 8$  and 1510 reflections with  $I > 3\sigma_I$ ,  $S = 1.15$ ,  $(\Delta/\sigma)_{\max} = 0.06$ . For  $\text{CrPcCl}_2$ ,  $\theta_{\max} = 22^\circ$ , 3662 measured reflections, 2575 independent in the range  $0 < h < 9$ ,  $0 < k < 15$ ,  $-10 < l < 10$  and 1162 with  $I > 3\sigma_I$ ,  $S = 2.74$ ,  $(\Delta/\sigma)_{\max} = 0.09$ . For  $\text{CoPcCl}_2$ ,  $\theta_{\max} = 23^\circ$ , 2080 measured reflections, 1408 independent in the range  $0 < h < 11$ ,  $0 < k < 16$ ,  $-9 < l < 9$  and 1225 with  $I > 3\sigma_I$ ,  $S = 1.32$ ,  $(\Delta/\sigma)_{\max} = 0.12$ . No significant variation of  $I$  (less than 1%). Structures solved by direct methods using *MULTAN* (Main, Woolfson & Germain, 1977). H atoms introduced at idealized positions in the calculation before last refinement cycles but not refined. Full-matrix refinement included anisotropic thermal parameters for non-H atoms. Final  $R = 0.036$  ( $wR = 0.044$ ) for  $\text{FePcCl}_2$ ,  $R = 0.048$  ( $wR = 0.091$ ) for  $\text{CrPcCl}_2$  and  $R = 0.031$  ( $wR = 0.037$ ) for  $\text{CoPcCl}_2$ ,  $w = 1/\sigma^2$ . Residual electron density between  $-0.3$  and  $+0.35 \text{ e } \text{\AA}^{-3}$ . Calculations performed on a PDP 11/44 computer using the *SDP* package (Frenz, 1978). Scattering factors from *International Tables for X-ray Crystallography* (1974); including anomalous-dispersion correction (Cromer, 1965).

The numbering system employed for carbons and nitrogens in the asymmetric unit of the structure is shown in Fig. 1.\* Packing of  $\text{MPcCl}_2$  is shown in Fig. 2.

**Discussion. Crystal structure.** Final positional and thermal parameters are presented in Tables 1, 2 and 3. The presented structures are the first examples in this series of high oxidation number molecules in which the metal resides at the center of the planar cation radical ligand. The only previous case reported is the dimeric  $\text{ZnPcCl}$  in which the metal is raised above the  $\text{Pc}^{+\cdot}$  plane by  $0.59 \text{ \AA}$  (Mossoyan-Deneux, Benlian, Pierrot, Fournel & Sorbier, 1985). As the symmetry around  $M$  is identical to that in parent  $\text{MPc}$ , comparisons are justified between the distances, similar standard deviations being observed. If significant, the observed differences will be related to the variations in the electron populations on  $M$  and  $\text{Pc}$ . This holds for  $\text{FePc}$  and  $\text{CoPc}$  only as no recent study is available for  $\text{CrPc}$  for comparison. The similarity of  $\text{CoPcCl}_2$  and  $\text{FePcCl}_2$  is remarkable; this favors the  $M^{\text{III}}\text{Pc}^+\cdot\text{Cl}_2$  formulation of these compounds stated in former papers (Myers *et al.*, 1975), rather than  $M^{\text{IV}}\text{PcCl}_2$ . The shortest distance from Cl to the next molecule's

peripheral hydrogen computed after final refinement is  $2.797 \text{ \AA}$  in  $\text{FePcCl}_2$  and  $2.804 \text{ \AA}$  in  $\text{CoPcCl}_2$ .

$\text{CrPcCl}_2$  appears different; its lattice is less compact, Cr—Cl and Cr—N distances are larger (Table 4), and Cl is at  $2.892 \text{ \AA}$  from the neighboring molecule.

**M—Cl distances:** these are well defined in the three complexes. A few results are present in the literature for similar Fe—Cl derivatives, but no comparison is possible for Co and Cr. Among the scarce reports on CrPc derivatives, the proposed  $(\text{CrPcFI}_x)_n$  is presented by Wynne & Nohr (1982) as a stacked polymer comparable to  $(\text{GaPcF})_n$  but no precise structural parameter available for reference is given. The only case with a pentacoordinate FePc derivative is reported by Palmer *et al.* (1985) with an out-of-plane iron and a bridging Cl—I—Cl ligand (Fe—Cl =  $2.320 \text{ \AA}$ ).

In  $\text{FePcCl}_2$  the shorter distance denotes a better overlap, consistent with our spectral results. On the other hand, Gans, Buisson, Duée, Marchon, Erler, Scholz & Reed (1986) report still shorter axial Fe—Cl bonds ( $2.168$ – $2.193 \text{ \AA}$ ) in porphyrin-radical-cation complexes; apart from five coordination the

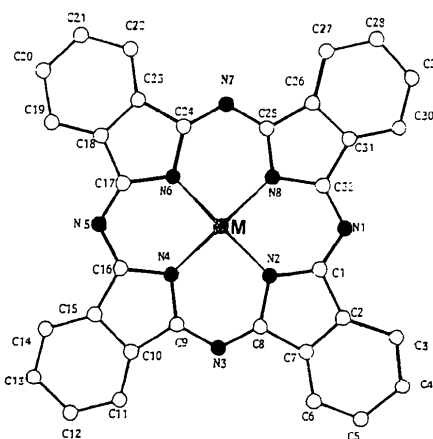


Fig. 1. Molecular structure and labeling scheme.

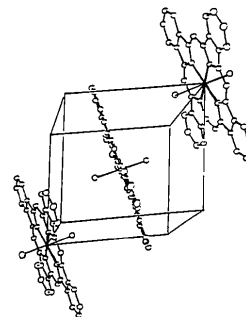


Fig. 2. ORTEP (Johnson, 1965) view along the  $b$  axis of the unit cell of  $\text{MPcCl}_2$ . Only three molecular units have been drawn for clarity.

\* Lists of structure factors, anisotropic temperature factors, H-atom coordinates, bond distances and angles involving H atoms, least-squares-planes data and thermal vibration r.m.s. amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52335 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates of CrPcCl<sub>2</sub> and equivalent isotropic temperature factors, with e.s.d.'s in parentheses
$$B_{\text{eq}} = \frac{1}{3}[B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$$

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Cl	0.4330 (2)	0.0315 (1)	1.2058 (2)	5.13 (5)
Cr	0.5000	0.0000	1.0000	4.06 (4)
C30	0.0576 (8)	0.2373 (6)	0.7989 (7)	4.9 (2)
N1	0.3887 (6)	0.2125 (4)	0.9110 (5)	4.5 (1)
C8	0.7398 (8)	0.1381 (5)	1.0543 (7)	4.2 (2)
C28	-0.1579 (8)	0.1404 (7)	0.7447 (8)	5.7 (2)
C32	0.2907 (8)	0.1459 (5)	0.8918 (7)	4.3 (2)
N3	0.8416 (6)	0.0794 (7)	1.1059 (5)	4.4 (1)
N2	0.5969 (6)	0.1199 (4)	1.0029 (5)	4.2 (1)
C1	0.5284 (8)	0.2007 (5)	0.9617 (7)	4.3 (2)
C7	0.7660 (8)	0.2368 (5)	1.0447 (6)	4.2 (2)
C25	0.1835 (8)	0.0096 (5)	0.8835 (7)	4.4 (2)
C6	0.8918 (9)	0.2879 (6)	1.0822 (7)	5.5 (2)
C3	0.6221 (9)	0.3674 (6)	0.9640 (8)	5.9 (2)
C27	-0.0786 (8)	0.0627 (7)	0.7863 (7)	4.9 (2)
C31	0.1347 (7)	0.1600 (5)	0.3876 (7)	4.3 (2)
C2	0.6356 (8)	0.2747 (5)	0.9863 (6)	4.4 (2)
C5	0.8750 (1)	0.3830 (6)	1.0582 (8)	6.3 (2)
C26	0.0676 (7)	0.0748 (5)	0.8321 (7)	4.1 (2)
C4	0.7449 (9)	0.4203 (6)	1.0010 (8)	6.2 (2)
C29	-0.0927 (9)	0.2264 (6)	0.7495 (7)	5.4 (2)
N8	0.3134 (6)	0.0545 (4)	0.9191 (6)	4.3 (1)

Table 3. Atom coordinates of CoPcCl<sub>2</sub> and equivalent isotropic temperature factors, with e.s.d.'s in parentheses
$$B_{\text{eq}} = \frac{1}{3}[B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$$

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Cl	0.4373 (1)	0.0304 (6)	1.2014 (9)	3.68 (2)
Co	0.5000	0.0000	1.0000	2.66 (1)
C30	0.0571 (4)	0.2375 (3)	0.7953 (3)	3.46 (8)
N1	0.3892 (3)	0.2125 (2)	0.9094 (3)	3.20 (6)
C8	0.7405 (4)	0.1368 (2)	1.0534 (3)	2.95 (7)
C28	-0.1602 (4)	0.1412 (2)	0.7396 (4)	4.00 (9)
C32	0.2915 (4)	0.1448 (2)	0.8918 (3)	2.86 (7)
N3	0.8441 (3)	0.0795 (2)	1.1066 (3)	3.28 (6)
N2	0.5951 (3)	0.1176 (2)	1.0025 (3)	2.78 (6)
C1	0.5297 (4)	0.1984 (2)	0.9604 (3)	2.98 (7)
C7	0.7688 (4)	0.2342 (2)	1.0421 (3)	3.01 (7)
C25	0.1836 (4)	0.0088 (2)	0.8838 (3)	3.03 (7)
C6	0.8952 (4)	0.2868 (3)	1.0791 (4)	3.90 (9)
C3	0.6234 (5)	0.3659 (3)	0.9584 (4)	4.22 (9)
C27	-0.0806 (4)	0.0623 (3)	0.7830 (4)	3.73 (9)
C31	0.1352 (4)	0.1601 (2)	0.8356 (3)	3.09 (8)
C2	0.6365 (4)	0.2735 (2)	0.9822 (3)	3.11 (8)
C5	0.8820 (5)	0.3801 (3)	1.0548 (4)	4.5 (1)
C26	0.0683 (4)	0.0734 (2)	0.8299 (3)	2.99 (7)
C4	0.7502 (5)	0.4186 (3)	0.9963 (4)	4.8 (1)
C29	-0.0941 (4)	0.2265 (3)	0.7456 (4)	3.75 (8)
N8	0.3160 (3)	0.0541 (2)	0.9206 (3)	2.81 (6)

Table 2. Atom coordinates of FePcCl<sub>2</sub> and equivalent isotropic temperature factors, with e.s.d.'s in parentheses
$$B_{\text{eq}} = \frac{1}{3}[B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$$

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Cl	0.4366 (1)	0.0309 (7)	1.2022 (1)	3.32 (2)
Fe	0.5000	0.0000	1.0000	2.47 (1)
C30	0.0560 (4)	0.2377 (3)	0.7944 (4)	3.22 (8)
N1	0.3882 (3)	0.2130 (2)	0.9087 (3)	3.00 (6)
C8	0.7403 (4)	0.1375 (3)	1.0531 (4)	2.80 (7)
C28	1.1608 (4)	-0.1406 (3)	1.2596 (4)	3.69 (9)
C32	0.2905 (4)	0.1453 (3)	0.8913 (4)	2.77 (7)
N3	0.8443 (3)	0.0799 (2)	1.1064 (3)	3.02 (7)
N2	0.5960 (3)	0.1185 (2)	1.0021 (2)	2.60 (6)
C1	0.5291 (4)	0.1993 (3)	0.9603 (4)	2.84 (7)
C7	0.7688 (5)	0.2355 (3)	1.0420 (4)	2.85 (7)
C25	0.8170 (4)	-0.0088 (3)	1.1163 (4)	2.79 (7)
C6	0.8955 (5)	0.2980 (3)	1.0795 (4)	3.60 (7)
C3	0.6227 (5)	0.3667 (3)	0.9588 (5)	3.98 (9)
C27	1.0813 (4)	-0.0622 (3)	1.2172 (4)	3.41 (9)
C31	0.1351 (4)	0.1599 (3)	0.8358 (4)	2.86 (8)
C2	0.6366 (4)	0.2743 (3)	0.9830 (4)	3.02 (8)
C5	0.8813 (5)	0.3808 (3)	1.0548 (5)	4.50 (1)
C26	0.9322 (4)	-0.0736 (3)	1.1698 (4)	2.85 (8)
C4	0.7496 (6)	0.4198 (3)	0.9966 (5)	4.06 (1)
C29	-0.0947 (5)	0.2261 (3)	0.7460 (4)	3.67 (9)
N8	0.3149 (3)	0.0540 (2)	0.9200 (3)	2.86 (6)

main difference is the distortion of the aromatic ligand from planar geometry, so that the way in which electronic populations around Fe are affected in the process of oxidation cannot be compared in the Pc and TPP series.

No major variation is expected between the Co and Fe complexes since the axial Co—Cl or Fe—Cl bond will be only slightly influenced in passing from the *d*<sup>6</sup> to *d*<sup>5</sup> configuration of the metal. CrPcCl<sub>2</sub> is

quite different; the 3*d* electron energy is weaker than in Fe and Co according to the calculation (Whangbo & Stewart, 1983) and further separated from the expected energy of the  $\pi$  system of the ligands. This explains a less stabilizing overlap with axial Cl; a much longer bond (2.34 Å) is observed.

*M*—*N* distances: differences are observed between the Cr and the very similar Fe and Co complexes. The same rationale based on the model by Whangbo & Stewart (1983) accounts for the differences: the Cr electrons are more localized and higher in energy than the ring  $\pi$  electrons whereas Co (and Fe) levels are much closer. This will result in better in-plane covalency for Fe (1.929–1.932 Å) and for Co (1.924–1.925 Å), than for Cr (1.96–1.98 Å). As a consequence of compensating effects, the *M*—*N* distance remains very comparable in CoPc, FePc, CoPcCl<sub>2</sub> and FePcCl<sub>2</sub>, around 1.92–1.93 Å, as it will be lengthened in going from *M*<sup>II</sup> to *M*<sup>III</sup>, whereas going from Pc to Pc<sup>+</sup> will shorten it. This shrinking of the N<sub>4</sub> square core of the phthalocyanine upon oxidation has already been observed, for instance, in the case of ZnPc (Mossoyan-Deneux, Benlian, Pierrot, Fournel & Sorbier, 1985).

C—C and C—N distances in the phthalocyanine ring: though planarity of the equatorial ligand is found in all cases within the limits of the computed standard deviation, noticeable variations in C—C and C—N distances clearly appear going from CoPc to CoPcCl<sub>2</sub> and from FePc to FePcCl<sub>2</sub>.

Based on the identical symmetry and allowing for the close experimental and treatment conditions, comparison of the structures of Pc and Pc<sup>+</sup> is

Table 4. Bond distances (Å) and selected bond angles (°)

	CrPcCl <sub>2</sub>	FePcCl <sub>2</sub>	CoPcCl <sub>2</sub>
M—C1	2.34 (1)	2.260 (1)	2.261 (1)
M—N2	1.98 (2)	1.929 (3)	1.924 (3)
M—N8	1.96 (3)	1.932 (3)	1.925 (2)
C30—C31	1.38 (1)	1.377 (5)	1.370 (5)
C30—C29	1.40 (1)	1.395 (5)	1.405 (5)
N1—C32	1.33 (2)	1.321 (5)	1.324 (4)
N1—C1	1.33 (2)	1.326 (5)	1.326 (4)
C8—N3	1.33 (2)	1.323 (4)	1.322 (4)
C8—N2	1.39 (2)	1.366 (4)	1.381 (4)
C8—C7	1.48 (1)	1.459 (5)	1.456 (5)
C28—C27	1.39 (1)	1.389 (6)	1.403 (5)
C28—C29	1.39 (1)	1.378 (4)	1.383 (6)
C32—C31	1.41 (1)	1.458 (5)	1.474 (5)
C32—N8	1.37 (2)	1.374 (5)	1.373 (4)
N2—C1	1.38 (1)	1.367 (5)	1.367 (4)
C1—C2	1.47 (1)	1.460 (5)	1.462 (5)
C7—C6	1.40 (1)	1.387 (4)	1.389 (6)
C7—C2	1.37 (1)	1.385 (5)	1.396 (5)
C25—C26	1.47 (1)	1.458 (6)	1.461 (5)
C25—N8	1.37 (2)	1.367 (4)	1.378 (5)
C6—C5	1.41 (2)	1.382 (6)	1.391 (6)
C3—C2	1.39 (1)	1.374 (6)	1.376 (5)
C3—C4	1.40 (1)	1.394 (4)	1.395 (6)
C27—C26	1.40 (1)	1.379 (5)	1.380 (5)
C31—C26	1.39 (1)	1.389 (6)	1.404 (5)
C5—C4	1.36 (1)	1.379 (4)	1.383 (4)
	CrPcCl <sub>4</sub>	FePcCl <sub>2</sub>	CoPcCl <sub>2</sub>
Cl—M—N8	89.7 (6)	89.9 (4)	89.8 (4)
Cl—M—N2	88.7 (6)	88.9 (3)	88.8 (3)
N2—M—N8	90.1 (4)	90.1 (1)	90.0 (2)
N1—C1—C2	124.1 (8)	122.1 (3)	121.6 (3)
N1—C1—N2	127.3 (8)	128.0 (4)	127.7 (4)
N2—C1—C2	108.5 (7)	109.9 (3)	110.7 (3)
C8—N2—C1	108.8 (7)	107.6 (3)	107.1 (3)
N3—C8—N2	126.7 (8)	128.0 (3)	120.0 (3)
C32—N1—C1	123.6 (8)	121.9 (3)	121.7 (3)

Table 5. Comparison of the bond distances (Å) in Pc and Pc<sup>+</sup> rings

	FePc <sup>a</sup>	FePcCl <sub>2</sub>	CoPc <sup>b</sup>	CoPcCl <sub>2</sub>
C1—C2	1.449 (2)	1.460 (5)	1.454 (4)	1.462 (5)
C7—C8	1.454 (2)	1.459 (5)	1.450 (3)	1.456 (5)
C2—C3	1.395 (2)	1.374 (6)	1.388 (3)	1.376 (5)
C4—C5	1.394 (3)	1.379 (4)	1.389 (5)	1.383 (4)
C3—C4	1.387 (3)	1.394 (4)	1.380 (5)	1.395 (6)
C5—C6	1.396 (3)	1.382 (6)	1.383 (4)	1.391 (6)
N1—C1	1.320 (2)	1.326 (5)	1.319 (4)	1.326 (4)
N3—C8	1.322 (2)	1.323 (4)	1.318 (4)	1.322 (4)

References: (a) Kirner, Dow & Scheidt (1976); (b) Williams, Figgis, Mason, Mason & Fielding (1979).

possible (Table 5). This is taken as a general trend rather than a conclusion for each particular bond. The differences are observed in three parts of the macrocycle. (i) The pyrrolic ring expands towards the center as C1—C2 and C7—C8 bonds are longer in MPcCl<sub>2</sub> than in MPc. (ii) The aza bridges become slightly longer in MPcCl<sub>2</sub> than in MPc. (iii) The benzo ring loses its sixfold symmetry as C2—C3 and C4—C5 are shorter while C3—C4 is longer than in MPc.

**Conductivity measurements.** Samples were selected from the larger (1–1.5 mm) and more regular crystals

(some of them had been reclaimed after SEM analysis) and mounted with gold wire on the four probe device already used in our previous studies (Mossoyan-Deneux, Benlian, Pierrot, Fournel & Sorbier, 1985; Mossoyan-Deneux, Benlian, Baldy & Pierrot, 1988). At each temperature, a few  $\mu\text{A}$  of current is applied at the end contacts and the potential is taken between the middle contacts. Due to the limited size of our single crystals the geometry of the polyhedron of which the resistance is measured is determined with a certain error in the distance between the gold wires stuck on the surface with silver lacquer and in the surface area of the cross section of the crystal. The error in  $R$  is negligible compared to that imposed by the micrometer and binocular used for the experiment. Therefore, we give  $\sigma$  values in a bracket of one order of magnitude. Typical experimental plots of  $R$  vs  $10^3/T$  are shown in Fig. 3. All conductivity values fall in the range of  $\sigma_{300} = 10^{-2}$ – $10^{-3} \Omega^{-1} \text{cm}^{-1}$  with small activation energies deduced from the resistance plots;  $E_a = 0.13$  (5) eV for CoPcCl<sub>2</sub>, CrPcCl<sub>2</sub> and FePcCl<sub>2</sub>. This is reminiscent of the observations on iodine-doped CrPcF (Wynne & Nohr, 1982) and would imply further investigation on the growth conditions in this case.

The electrical behavior of these solids can be explained by the established structures. The stacking in the cell does not allow an efficient overlap between adjacent aromatic rings, neither does the tilted orientation of the molecular unit. On the other hand, large sized Pc<sup>+</sup> radicals will allow intermolecular

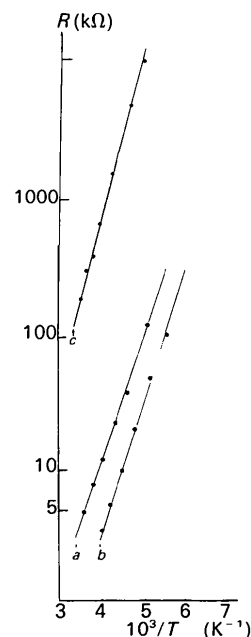


Fig. 3. Sample plots of  $R$  vs  $10^3/T$  for crystals of: (a) FePcCl<sub>2</sub>, (b) CoPcCl<sub>2</sub> and (c) CrPcCl<sub>2</sub>.

mobility of electrons between the half occupied  $\pi$  levels. The rather weakly bound halogens are not located too far from the aromatic part of the adjacent molecules so that their relatively easy libration would add a cooperative action to the process of electron hopping favored by lattice fluctuations, hence the rather high conductivity of the materials compared to the figures given for the starting MPC complexes ( $10^{-12}$ – $10^{-10} \Omega^{-1} \text{cm}^{-1}$ ).

In our crystals, the integral valence state is confirmed by elemental analyses on the crystalline samples at the SEM which all gave  $\text{Cl}/M = 2$ . This is consistent with the semiconductor type of the resistance plots. These are very reproducible from batch to batch and with time, giving a constant value for  $E_a$ . The semiconductor behavior has commonly been observed in integral valence complexes giving stacked molecular crystals (Palmer *et al.*, 1986) but this does not give evidence for the intrinsic nature of the charge carriers. The half filled  $\pi$  level of the aromatic system is in favor of that type of mechanism, though one cannot exclude some degree of doping involved in the conduction in these samples. The integral valence is based on the fact that within the limit of the residual electron density in the lattice at the end of the refinement, no inserted anion or extraneous atom is detected. An enhanced conduction resulting from artifactual insertion of dopants would not be constant with time and/or would give broken lines in the resistance plots and scattered values for the experimental activation energy from sample to sample.

Three isostructural complexes have been characterized under identical conditions. The position of the metal at the center of symmetry and the planarity of the ligand are major differences with the case of comparable oxidized metalloporphyrins in which oxidation induces lowering of overall symmetry and distortion of the ligand.

The solids behave as semiconductors with no transition in the temperature range of this study (170–300 K); the experimental conductivities,  $\sigma_{300} = 10^{-2}$ – $10^{-3} \Omega^{-1} \text{cm}^{-1}$ , are comparable to those of integral-valence donor–acceptor molecular crystals. The activation energy deduced from experimental plots is low [0.13 (5) eV]. From the structure, one can infer a rather low mobility of carriers. The CrPcCl<sub>2</sub> complex which we have prepared and studied appears to be different from the earlier reported derivatives of CrPc obtained by chemical doping.

A unique model described as  $M^{\text{III}}\text{Pc}^{+\cdot}$  is consistent with the electronic energies of the metals in all three cases, with less stabilizing metal–ligand overlaps and a slightly looser packing of the lattice in CrPcCl<sub>2</sub> than in CoPcCl<sub>2</sub>/FePcCl<sub>2</sub>. Confirmation will be given by magnetic and resonance studies. These preliminary results do not allow a proposal for the

conduction mechanism and call for more experiments on larger crystals.

This crystallographic study was performed in the Laboratoire de Cristallographie (Faculté St Jérôme-Marseille). We are very grateful to Dr Marcel Pierrot for efficient help and fruitful discussions.

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## Structures of (I) Bis[benzylmethyl(phenyl)ammonium] Tetrachloromanganate(II) and (II) Bis[benzylmethyl(phenyl)ammonium] Tetrachlorocobaltate(II)

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**Abstract.** (I):  $[\text{C}_{15}\text{H}_{18}\text{N}]_2[\text{MnCl}_4]$ ,  $M_r = 621.4$ ,  $a = 13.150$  (6),  $b = 14.105$  (8),  $c = 16.694$  (8) Å,  $V = 3095$  (5) Å<sup>3</sup>,  $D_m = 1.35$ ,  $D_x = 1.33$  Mg m<sup>-3</sup>,  $\mu = 0.812$  mm<sup>-1</sup>,  $F(000) = 1292$ , final  $R = 0.041$  for 967 'observed' reflections. (II):  $[\text{C}_{15}\text{H}_{18}\text{N}]_2[\text{CoCl}_4]$ ,  $M_r = 625.4$ ,  $a = 13.040$  (4),  $b = 14.085$  (9),  $c = 16.450$  (5) Å,  $V = 3021$  (4) Å<sup>3</sup>,  $D_m = 1.38$ ,  $D_x = 1.37$  Mg m<sup>-3</sup>,  $\mu = 0.964$  mm<sup>-1</sup>,  $F(000) = 1300$ , final  $R = 0.044$  for 1091 'observed' reflections. Both (I) and (II): orthorhombic,  $C22_1$ ,  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $T = 298$  K. The two complexes are isomorphous. The conformation of the N<sup>+</sup>—C—C—C part of the cation is *gauche* and is unaffected by the presence of the bulky anions. The metal ions have almost perfect tetrahedral geometry. The crystal structures are stabilized by Coulombic and van der Waals forces.

**Introduction.** Quaternary amines are active at the cholinergic junctions, their pharmacological activities

being correlated with their conformations. It has been found that benzylmethyl(phenyl)ammonium chloride has close conformational similarity to the quaternary amine acetylcholine and its structural analogues (Chaudhuri, Banerjee, Deb Purkayastha, Sen Sarma & Bocelli, 1987). The present study was undertaken to study the effect of the presence of bulky anions, like  $\text{MnCl}_4^{2-}$  and  $\text{CoCl}_4^{2-}$ , on the conformation of benzylmethyl(phenyl)ammonium.

**Experimental.** Pale green crystals of Mn complex (I) and deep blue crystals of Co complex (II) from hot methanol, density by flotation (benzene–bromoform mixture), crystal size (I)  $0.15 \times 0.15 \times 0.19$  mm and (II)  $0.13 \times 0.17 \times 0.21$  mm, Siemens AED diffractometer, Zr-filtered Mo  $K\alpha$  radiation, accurate cell parameters from least-squares fit of setting angles of (I) 27 reflections ( $8 \leq \theta \leq 20^\circ$ ) and (II) 25 reflections ( $10 \leq \theta \leq 22^\circ$ ) using the *CTDIF* routine (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979),  $C22_1$  (systematic absences:  $hkl$ ,  $h+k$  odd;  $00l$ ,  $l$  odd), 2109 unique reflections measured for (I) and 2017 for (II) ( $2 \leq \theta \leq 30^\circ$ ,  $0 \leq h \leq 18$ ,  $0 \leq k \leq 19$ ,  $0 \leq l \leq 23$  for

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