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Structures of Becton's [$Pt(NH_3)_4CuCl_4$] and Millon's [$Cu(NH_3)_4PtCl_4$] Salts*

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The room-temperature crystal structures of Becton's and Millon's salts have been shown not to be isostructural, as previously believed, and have been refined by the full-matrix least-squares method using three-dimensional Mo $K\alpha$ intensity data. Becton's salt crystallizes in a cell of $P2_1/c$ symmetry with a_0 = 7·687 (2), b_0 = 7·941 (2) and c_0 = 8·057 (2) Å and β = 91·61 (1)° while Millon's salt is isomorphous with Magnus's green salt, $Pt(NH_3)_4PtCl_4$, with $P4/mnc$ symmetry and dimensions a_0 = 9·036 (3) and c_0 = 6·441 (2) Å. The structure of Millon's salt (R = 0·029) consists of $Cu(NH_3)_4^{2+}$ and $PtCl_4^{2-}$ square-planar ions alternating in stacks along the c axis with 2·298 (4) Å Pt–Cl and 2·00 (1) Å Cu–N separations; that for Becton's salt (R = 0·038) consists of square-planar $Pt(NH_3)_4^{2+}$ ions, with 2·03 (1) and 2·05 (1) Å Pt–N separations, and infinite copper–chloride ion layers with the typical distorted octahedral copper environment of four shorter [2·271 (3) and 2·302 (4) Å] and two longer [3·257 (4) Å] Cu–Cl separations.

Introduction

Shortly after the crystal structure of Magnus's green salt [$Pt(NH_3)_4PtCl_4$], determined by Atoji, Richardson & Rundle (1957; all references, when subsequently cited, will employ only initials plus year), was shown to consist of square-planar $Pt(NH_3)_4^{2+}$ and $PtCl_4^{2-}$ ions stacked upon each other with 3·25 Å metal–metal interactions, attention was directed towards the mixed copper–platinum system. Bukovska & Porai-Koshits (1960) suggested that the two isomers $Cu(NH_3)_4PtCl_4$ and $Pt(NH_3)_4CuCl_4$, known as Millon's and Becton's salts, respectively, had the same crystal structure and were isomorphous with Magnus's green salt. Studies on the stereochemistry of copper by spectral techniques (Dudley, Hathaway, Hodgson, Mulcahy & Tomlinson, 1974; Harlow, Wells, Watt & Simonsen, 1974) have noted that these compounds do not properly fit trends established by other $Cu(NH_3)_4^{2+}$ or $CuCl_4^{2-}$ compounds; however, such departures usually are attributed to small differences in the interatomic separation arising from the usual difficulties experienced with materials containing high atomic number elements, in this case platinum. Furthermore, e.p.r. data on Becton's salt were at variance with the suggested crystal structure (Soos, 1974). Our structure studies on these two salts show that these materials are not isostructural.

Experimental details and results

Powder samples of Becton's salt were prepared for analysis by mixing saturated aqueous solutions of $CuCl_2.2H_2O$ and $Pt(NH_3)_4Cl_2$ (Engelhard) in equimolar ratios. The resulting solution was cooled in ice and concentrated hydrochloric acid was added dropwise until no further precipitation was observed. The green microcrystalline powder was filtered, washed with small amounts of methanol and ether, and dried under vacuum. Analysis: calculated for $CuPtN_4H_{12}Cl_4$: Cu 13·56; Pt 41·63; N 11·96; H 2·59; Cl 30·26%. Found: Cu 12·95; Pt 42·46; N 11·80; H 2·67; Cl 29·08%. Larger single crystals were grown by diffusion through gels. This technique was necessary because simple diffusion resulted in small crystals which were of poor quality and were contaminated with a brown byproduct. Higher quality crystals were obtained when solutions of $CuCl_2.2H_2O$ and $Pt(NH_3)_4Cl_2$ in 2·2 *M* HCl were connected by a 30 cm U-tube containing a gel prepared from sodium silicate and aqueous HCl (Henisch, 1970) and allowed to diffuse for 37 days at 5°C.

Deep-purple needles (maximum size about 3 × 0·2 mm) of Millon's salt were prepared by diffusion of dilute aqueous solutions of K_2PtCl_4 (0·10 g in 5 ml of water) and $Cu(NH_3)_4SO_4$ (0·06 g in 4 ml of water plus 1 ml of concentrated ammonia solution) at 4°C for five days into opposite ends of a 12 cm tube containing 11 ml H_2O.

Crystals were examined by X-ray photographic techniques to insure that single-crystal specimens were selected for our measurements. The space group for Becton's salt was uniquely defined on the basis of the observed extinctions on Mo $K\alpha$ precession photographs as $P2_1/c$; for Millon's salt, the centrosymmetric $P4/mnc$ rather than noncentrosymmetric $P4nc$ was selected and confirmed by the excellent agreement of the final calculated and observed structure factors.

The lattice constants determined on a Picker diffractometer with Mo $K\alpha$ radiation were a_0 = 7·687 (2),

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b_0=7·941 (2), c_0=8·057 (2) Å and β=91·61 (1)° with a cell volume V=491·6 Å^3 for Becton's salt and a_0= 9·036 (3) and c_0=6·441 (2) Å with V=525·9 Å^3 for Millon's salt. The θ–2θ scan technique and a scintillation detector employing pulse-height discrimination were used to measure the Mo $K\alpha$ intensity data to 55° 2θ. On Becton's salt, a complete hemisphere of measured intensities yielded 852 observed and 279 'less than' intensities while on Millon's salt an octant yielded 273 observed and 62 'less than' intensities when averages were taken on pairs of symmetry equivalent *hkl* reflections. The average value for the intensities with values greater than $3\sigma_{(\text{ave.})}/\sqrt{n}$, where $\sigma_{(\text{ave.})}$ is the average σ for n measurements and where $\sigma=A[(N_{\text{sc}}+K^2N_B)]^{1/2}$ and A, N_{sc}, N_B and K are the absorption correction, total scan count, background counts and the time ratio of the scan to background, respectively, were those considered observed. Scattering factors and dispersion corrections were taken from Tables 3.3.1A and 3.3.2C of *International Tables for X-ray Crystallography* (1962). Initial parameters for Millon's salt were taken from those of Magnus's green salt while those for Becton's salt were deduced from symmetry considerations and Fourier syntheses, and intensity data were subjected to least-squares refinement using isotropic, followed by anisotropic, thermal parameters. The function $w(F_o-F_c)^2$ was minimized with $w=n/\sigma_{(\text{ave.})}^2$. The final difference Fourier synthesis did not clearly show positions of the hydrogen atoms about the ammine groups; peaks equivalent to two electrons remained very close to the location of the platinum ion in both compounds. Final residual values, $R=\sum||F_o|-|F_c||/\sum|F_o|$, on observed data were 0·038 and 0·029 for Becton's and Millon's salts, respectively.* The resulting positional and thermal parameters are given in Table 1. Computations were performed with the X-RAY 72 System (Stewart, 1972).

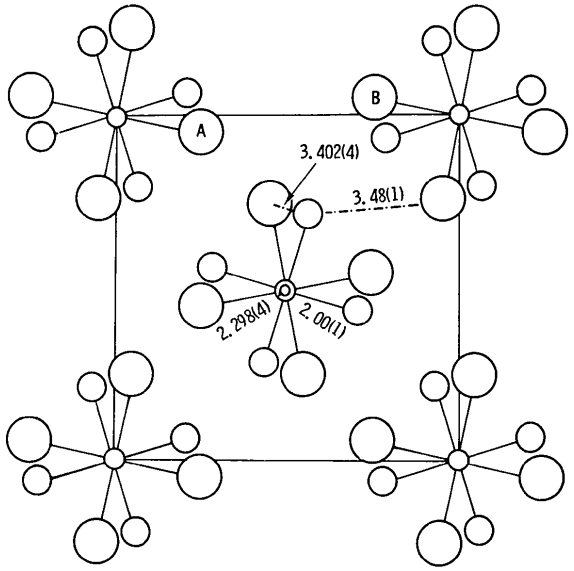

Fig. 1. Projection of the structure of Millon's salt along the tetragonal c axis. Positions of Pt, Cu, N and Cl atoms are indicated by circles of increasing size. In this crystal structure, the square-planar $Cu(NH_3)_4^{2+}$ and $PtCl_4^{2-}$ ions lie on mirrors at $z=0$ and $\frac{1}{2}$; these ions alternately stack upon each other. The Cu–Pt separation is equal to $\frac{1}{2}c$ (3·22 Å). The probable arrangement for hydrogen bonding (dot-dash) is indicated on only one of the nitrogen atoms and consists of two 3·402 Å separations to chloride ions in the stack and very likely of one 3·48 Å separation to an adjacent stack. The next closest separations to this nitrogen atom are to chloride ion A (3·50 Å) and B (3·56 Å).

The values for the interatomic separations and angles for Millon's salt are shown on Fig. 1. Symmetry requires that both ions be exactly square planar. The 2·00 Å value for the Cu–N separation appears to fit previous spectral (DHHMT, 1974) and structural (Morosin, 1969) correlations for such separations better than the previous value of 2·04 Å (BP-K, 1960); the 2·298 Å Pt–Cl separation is shorter than the earlier reported value of 2·36 Å (BP-K, 1960) as well as the 2·34 Å (ARR, 1957) reported in Magnus's green salt. Hydrogen bonding shown in Fig. 1 links the nitrogen groups to the chloride ions within the stacking sequence as well as to those on an adjacent stack. The longer separation to the adjacent stack is not as

Table 1. *Positional and thermal parameters*

U_{ij} are of the form $\exp(-2\pi^2\sum U_{ij}h_ih_ja_i^*a_j^*)$ in units of 10^{-2} Å^2.

(*a*) Becton's salt

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	$\frac{1}{2}$	0	$\frac{1}{2}$	0·86 (3)	1·20 (3)	1·49 (3)	−0·16 (3)	−0·20 (2)	0·01 (3)
Cu	0	0	0	1·98 (10)	2·39 (10)	1·72 (9)	−0·44 (10)	−0·22 (7)	−0·03 (10)
Cl(1)	−0·0103 (5)	−0·0356 (4)	0·2792 (4)	3·2 (2)	2·5 (2)	1·6 (1)	−0·4 (1)	−0·2 (1)	0·1 (1)
Cl(2)	0·2068 (4)	0·2073 (4)	0·0368 (4)	1·9 (1)	2·6 (2)	2·6 (2)	−0·7 (1)	−0·3 (1)	−0·1 (1)
N(1)	0·519 (2)	−0·032 (2)	0·251 (2)	3·5 (7)	3·1 (8)	2·8 (6)	0·6 (6)	0·0 (5)	0·5 (5)
N(2)	0·317 (1)	0·184 (1)	0·459 (2)	1·7 (5)	1·9 (6)	3·6 (7)	0·4 (4)	−0·7 (5)	0·0 (5)

(*b*) Millon's salt

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0	0	0	2·08 (3)	U_{11}	2·15 (5)	0	0	0
Cu	$\frac{1}{2}$	$\frac{1}{2}$	0	1·89 (8)	U_{11}	2·60 (14)	0	0	0
Cl	0·0572 (4)	0·2477 (4)	0	3·6 (2)	2·4 (2)	4·3 (2)	−0·2 (1)	0	0
N	0·559 (1)	0·713 (1)	0	3·6 (7)	2·5 (7)	4·8 (8)	0·4 (5)	0	0

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31049 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

favorably oriented with respect to those within the one-dimensional stack; the hydrogen-bonding network very likely involves a bifurcated bond which also includes chloride ion *B*.

Becton's salt consists of square-planar $Pt(NH_3)_4^{2+}$ ions and infinite copper chloride ion layers with the typically distorted octahedral copper environment of four shorter (2·271 and 2·302 Å) and two longer (3·257 Å) separations [Fig. 2; angles involving the longer Cu–Cl separation are Cl(1)–Cu–Cl(2′) 92·6 (1), Cl(2)–Cu–Cl(2′) 92·6 (1) and Cu–Cl(2)–Cu 167·4 (1)°]. Such a two-dimensional layer has been observed in various substituted ammonium copper chloride compounds, by structure determinations on $(NH_4)_2CuCl_4$ (Willett, 1964), $(C_2H_5NH_3)_2CuCl_4$ (Steadman & Willett, 1970), $(C_3H_5NH_3)_2CuCl_4$ (Barendregt & Schenk, 1970), $(C_6H_5NH_3)_2CuCl_4$ (Larsen, 1974), $(NH_3C_2H_4NH_3)CuCl_4$ (Birrell & Zaslow, 1972) and $(NH_3CH_2CH_2)_2NH_2CuCl_5$ (Ferguson & Zaslow, 1971) as well as by magnetic measurements on compounds of the general formula $(C_nH_{2n+1}NH_3)_2CuX_4$ with n as large as 10 and X = Cl, Br or mixtures thereof (Bloembergen & Miedema, 1974). In the above mentioned compounds the short distances span 2·272–2·332 Å while the longer set span 2·793–3·04 Å [a linear chain system with a 3·10 Å separation has been reported by Anderson & Willett (1974)]. The separation between these copper–halide layers increases with substitution of larger groups on the ammonium ion; this separation in Becton's salt is only 4% larger than that of $(NH_4)_2CuCl_4$. The Pt–N separations are in good agreement with the 2·06 Å values found in Magnus's green salt. The hydrogen bond network in our compound is not clear from the near-neighbor contact separations (Fig. 2). For N(1) the five similar values suggest that bifurcated bonds may be very likely. In the case of N(2), two of the separations are somewhat shorter than the remaining values, which suggests that these separations are probably along the hydrogen bond; in addition N(2) is only 3·52 Å away from an adjacent platinum ion. The $Pt(NH_3)_4^{2+}$ ions are square-planar within the standard deviations of this determination. The closest approach to the ion involves N(2) atoms mentioned above and chloride ions at 4·09 Å.

An interesting aspect concerns the cell volumes of these two salts. The volume for Becton's salt is about 7% smaller than that for Millon's salt even though the square-planar ions are stacked closer together (3·22 Å) in the latter compound than the 3·257 Å separation in the copper-chloride ion layers. Evidently the packing in two dimensions for one half of the ions is more efficient than that for all the ions in only one dimension.

Discussion

The coordination about copper(II) has always provoked discussion; in particular, in a distorted octahedral environment with its usual four short and two longer bonds, the question arises as to how long must these latter 'bonds' be before one clearly has a case for a square-planar environment. It is our conjecture that even in Becton's salt, with the longest Cu–Cl interaction known to us, the correct environment is a distorted octahedron. This premise is partially based on the fact that with one known exception all copper compounds with four close ligands will either possess an environment in which (*a*) at least one of the two octahedral positions is filled by a more distant ligand (and then the copper ion is usually displaced towards it), or (*b*) both octahedral sites are filled by more distant ligands, or (*c*) an environment best described as distorted tetrahedral. In the cases of either distorted octahedral or tetrahedral, structurally similar materials with other divalent ions (namely Mn^{2+} and Zn^{2+}) in more nearly regular environments are known. For the above-mentioned substituted ammonium copper chloride compounds, the structural details have been reported for only one of the corresponding manganese compounds $(C_3H_7NH_3)_2MnCl_4$ (Peterson & Willett, 1972), which is found to be very similar in overall crystal structure and in which the four Mn–Cl separa-

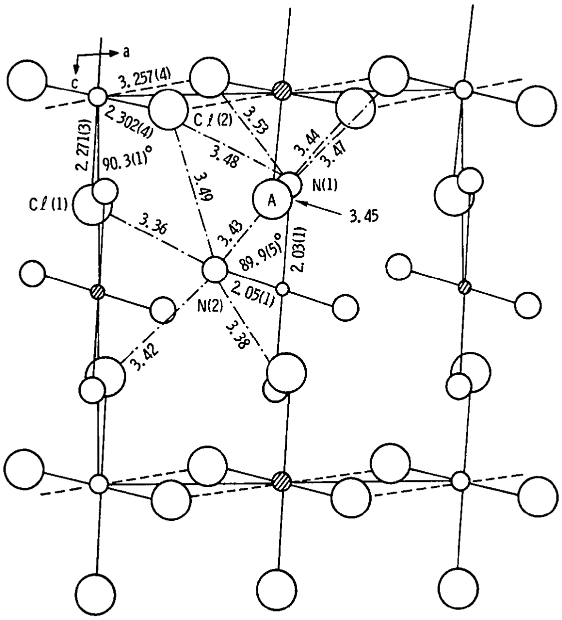

Fig. 2. Projection of the structure of Becton's salt along the monoclinic *b* axis. Positions for Pt, Cu, N and Cl atoms are indicated using increasing size of circles; metal atoms at $y=\frac{1}{2}$ are shaded. In this crystal structure layers of copper-chloride ions are separated by $Pt(NH_3)_4^{2+}$ ions. These entities are held together by a network of hydrogen bonds. The close nitrogen-chloride ion separations ($\sigma = 0·01$ Å) are indicated with dot-dash lines; N(1) has five such separations of approximately equal length, suggesting that bifurcated bonds are very likely; for N(2) five separations are also shown with two certainly shorter than the remaining values. The platinum at $0,\frac{1}{2},\frac{1}{2}$ is 3·52 Å from N(2) and 4·09 Å from Cl(*A*); from the angles formed, *i.e.* N(1)–Pt–N(2′) of 85·9 (1)° and N(2)–Pt–N(2′) of 87·1 (1)°, it would appear N(2)′ is better situated to fill a very remote distorted octahedral position involving the Pt.

tions within the layer are identical by symmetry and those perpendicular to the layer are shorter. The only known exception in which a truly square planar discrete $CuCl_4^{2-}$ ion exists has only recently been reported with 2·248 (1) and 2·281 (1) Cu–Cl separations (HWWS, 1974).

For the above-mentioned copper compounds, we have attempted to correlate the length of these longer Cu–Cl separations with the shorter Cu–Cl separations, realizing, of course, the effects that hydrogen bonding probably induces in such bonds. No relationship is noted for either the Cu–Cl separation in the layer or that perpendicular to the layer with respect to these longer Cu–Cl separations. However, if one employs the *average* values for the shorter Cu–Cl separations, a smooth curve can be drawn through the values, with the largest departure being about 4σ (data of FZ, 1971). Even the data on the exception noted above (HWWS, 1974) appear reasonable in such a plot.

Finally, we believe the resulting structure for Becton's salt also strengthens our conjecture. There must be some weak interaction *via* this long 3·257 Å separation for the material to crystallize with the neighboring chloride ion oriented to fill the distorted octahedral position. Otherwise an arrangement isomorphous with Millon's salt would have been equally favorable.

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The Crystal Structure of Dioxygentetra(dimethylphenylarsine)rhodium(I) Perchlorate

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Dioxygentetra(dimethylphenylarsine)rhodium(I) perchlorate is triclinic with $a=13{\cdot}24$ (2), $b=17{\cdot}42$ (2), $c=10{\cdot}30$ (2) Å, $\alpha=89{\cdot}9$ (1), $\beta=87{\cdot}9$ (1), $\gamma=128{\cdot}6$ (1)°, $Z=2$, space group $P\bar{1}$. Least-squares refinement with counter data decreased R to 0·060. The coordination about Rh is trigonal bipyramidal, considering dioxygen as a monodentate ligand, which is usual for this class of complex. The O–O bond length of 1·46 (2) Å is in the range predicted for irreversible dioxygen uptake. Rh–As distances were found to be between 2·418 and 2·471 (6) Å.

Introduction

A growing interest exists in organometallic complexes in which small covalent molecules such as dioxygen are directly coordinated to the transition metal atom (Valentine, 1973). X-ray crystallographic determinations on Rh and Ir dioxygen complexes (McGinnety, Payne & Ibers, 1969) to study the effects of changing the metal atom and the ligands on the O–O bond length, have suggested that long O–O bonds (up to 1·63 Å) are associated with irreversible metal–dioxygen bonding. The recent structure of the reversible dioxygen adduct $IrO_2Cl(CO)\,[P(C_2H_5)\,(C_6H_5)_2]_2$ proved, however, to be anomalous (Weininger, Taylor & Amma, 1971). The observed O–O length of 1·46 Å approached the range anticipated for irreversible dioxygen uptake. We thus decided to determine the structure of the known (Haines & Singleton, 1971; Haines, 1971) complex $\{RhO_2[As(CH_3)_2C_6H_5]_4\}\,\{ClO_4\}$ which contains irreversibly bonded dioxygen. A com-