piled and amended by the Kyoto University authors for special use on mini/microcomputers.

Discussion. All interatomic distances and bond angles are normal. For example, Mg—O distances are between 2.055 and 2.114 Å and the deviation of O—Mg—O angles from 90 or 180° is less than 9.32°. The *b* projection of the unit cell is presented in Fig. 1. We can see that the crystal has a double-layer structure: one is the $[Mg(HCO_2)_2]_\infty$ network and the other is an assembly of urea molecules. Interlayer bonding is achieved through hydrogen bonds (See Table 2).

A projection of the $[Mg(HCO_2)_2]_\infty$ network on the *ab* plane along the *c* direction is shown in Fig. 2. Both magnesium ions are surrounded octahedrally by four square-planar O atoms belonging to different formate ions and by two O atoms of urea molecules. The formate ion bridge between neighboring Mg ions is of the so-called *anti-anti* type seen between *A*-site ions in $Mg(HCO_2)_2.2H_2O$ (Osaki, Nakai & Watanabe, 1964). The two molecular planes of the urea coordinated to an Mg^{2+} ion are nearly perpendicular to each other.

It is interesting that the monoclinic Mg lattice can be interpreted as an approximate body-centered tetragonal lattice because $a \simeq b$ and $2c|\cos\beta| = 16.555 \simeq a$.

References

Deguchi, H., Hoshiko, T., Takeda, K. & Yamagata, K. (1990). *J. Magn. Magn. Mater.* **90/91**, 303–304.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Osaki, K., Nakai, Y. & Watanabe, T. (1964). *J. Phys. Soc. Jpn*, **19**, 717–723.

Takeda, K., Deguchi, H., Hoshiko, T. & Yamagata, K. (1989). *J. Phys. Soc. Jpn*, **58**, 3489–3492.

Yamagata, K., Saito, Y., Abe, T. & Hashimoto, M. (1989). *J. Phys. Soc. Jpn*, **58**, 3865–3866.

Yamagata, K., Saito, Y., Abe, T. & Hashimoto, M. (1990). *J. Magn. Magn. Mater.* **90/91**, 299–300.

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Structure of 1,2,3-Tris(dimethylamino)cyclopropenylium Hexachloroniobate(V) and Hexachlorotantalate(V)

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Abstract. (1) $[C_9H_{18}N_3][NbCl_6]$, $M_r = 473.89$, rhombohedral, $R\bar{3}$, $a = 12.7898$ (6), $c = 19.0879$ (9) Å, $V = 2704$ Å^3, $Z = 6$, $D_x = 1.746$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.70926$ Å, $\mu = 15.291$ cm^{-1}, $F(000) = 1416$, room temperature, final $R = 0.025$ for F and 862 reflections. (2) $[C_9H_{18}N_3][TaCl_6]$, $M_r = 561.93$, rhombohedral, $R\bar{3}$, $a = 12.8180$ (3), $c = 19.1170$ (7) Å, $V = 2720$ Å^3, $Z = 6$, $D_x = 2.058$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.70926$ Å, $\mu = 68.763$ cm^{-1}, $F(000) = 1608$, room temperature, final $R = 0.023$ for F and 862 reflections. The structures are isomorphic. The crystal structure consists of layers parallel to the *ab* plane; the interaction between anions and cations occurs in the **c** direction thus forming columns distributed in rhombohedral sequence.

Introduction. The structure of the tris(dimethylamino)cyclopropenylium ion has been reported by Ku & Sundaralingam (1972). Our structure determination is part of investigations on the salts of the tris(dimethylamino)cyclopropenylium ion and inorganic complex anions (Yoshida & Tawara, 1971; Weiss & Schloter, 1975). In several cases these salts show – as do the title compounds – interesting outer-sphere charge-transfer interactions between cation and anion leading to intensely coloured solids although the ionic components of the salts are colourless (Weiss, 1979).

Experimental. In an N_2 atmosphere 576 mg $NbCl_5$ was dissolved in a mixture of 20 ml dry CH_3CN and 0.5 ml $SOCl_2$. A solution of 434 mg tris(dimethyl-

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amino)cyclopropenylium chloride in 20 ml CH_3CN was added. After stirring for 2 h the resulting mixture was filtered. Cooling the filtrate to 263 K led to dark-blue crystals of compound (1). The specimen used for the structure determination had dimensions 0.25 × 0.3 × 0.3 mm.

In an N_2 atomsphere 1271 mg $TaCl_5$ was dissolved in a mixture of 15 ml dry CH_3CN and 0.5 ml $SOCl_2$. A solution of 723 mg tris(dimethylamino)cyclopropenylium chloride in 10 ml CH_3CN was added. After stirring for 2 h the resulting mixture was filtered. Cooling the filtrate to 263 K led to dark-red crystals of compound (2). The specimen used for the structure determination had dimensions 0.2 × 0.2 × 0.4 mm.

All measurements were performed on a PW 1100 instrument rebuilt and equipped with additional facilities (M. Gomm, 1991; private communication). Measurements by ω–2θ scan, graphite-monochromated Mo $K\alpha$ radiation, modified Lehmann–Larsen profile analysis; lattice parameters derived from 68 reflections with $6 \leq \theta \leq 14°$; absorption correction by using a modified version of the program *CAMEL JOCKEY* (Flack, 1975) based on empirical ψ-scan data, maximum and minimum correction factors 1.20 and 1.30 for structure (1), 0.80 and 1.40 for structure (2). Intensities collected for $-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-21 \leq l \leq 21$, $\theta_{\max} = 23°$; six standard reflections, no significant variation; 6882 reflections measured, 862 unique reflections, no unobserved reflections omitted; $R_{\rm int}$ based on F was 0.015 for structure (1) and 0.012 for structure (2).

The Nb, Ta and Cl atoms were determined using the Patterson method. The remaining non-H atoms were determined from a Fourier map. A subsequent difference Fourier map revealed all H atoms. Full-matrix least-squares refinement based on F; weights derived from experimental standard deviations, $w = 1/\sigma(F)$. In the final stage anisotropic displacement parameters were used for all non-H atoms and isotropic displacement parameters for the H atoms.*

The final R values for structure (1) were: $R = 0.025$, $wR = 0.028$, $S = 1.80$, ratio of maximum shift to e.s.d. = 0.01. The final R values for structure (2) were: $R = 0.023$, $wR = 0.025$, $S = 1.75$, ratio of maximum shift to e.s.d. = 0.01. Maximum and minimum electron density residuals: $\Delta\rho_{\max} = 0.85$, $\Delta\rho_{\min} = -0.71$ e Å^{-3} for structure (1) and $\Delta\rho_{\max} = 0.70$, $\Delta\rho_{\min} = -0.65$ e Å^{-3} for structure (2). Extinction corrections were applied according to the Zachariasen (1968) formula; maximum extinction factor was 2.02 for structure (1) and 1.80 for structure (2); form-factor tables from *International Tables for X-ray Crystallography* (1962, Vol. III). All computations were performed on a MicroVAX II computer using an adapted version of the program system *ATARI CRYSTAN*88 (1989).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for structures* (1) *and* (2)

Occupancy of atoms = 1.0.

	x	y	z	$U_{\rm eq}$
Nb(1)	0.000	0.000	0.000	0.0364
Nb(2)	0.000	0.000	0.500	0.0456
Cl(3)	0.09447 (6)	0.17218 (6)	0.07109 (5)	0.0469
Cl(4)	0.16237 (9)	0.0326 (1)	0.42973 (6)	0.0926
C(5)	0.0701 (2)	0.0212 (2)	0.2429 (1)	0.0374
N(6)	0.1868 (2)	0.0577 (2)	0.2425 (1)	0.0469
C(7)	0.2748 (4)	0.1842 (3)	0.2529 (3)	0.0628
C(8)	0.2251 (5)	0.9694 (5)	0.2502 (3)	0.0642
Ta(1)	0.000	0.000	0.000	0.0311
Ta(2)	0.000	0.000	0.500	0.0396
Cl(3)	0.09450 (9)	0.17190 (9)	0.07094 (7)	0.0476
Cl(4)	0.1620 (1)	0.0325 (2)	0.42972 (9)	0.0931
C(5)	0.0695 (4)	0.0210 (2)	0.2428 (2)	0.0364
N(6)	0.1861 (2)	0.0577 (2)	0.2428 (2)	0.0450
C(7)	0.2733 (5)	0.1847 (5)	0.2527 (4)	0.0642
C(8)	0.2261 (5)	−0.0308 (6)	0.2499 (4)	0.0595

Table 2. *Interatomic distances* (Å) *and angles* (°) *for structures* (1) *and* (2)

The indicated operation, centring and translation refer to the atoms on the right. Symmetry operations (centrings: 000; $\frac{2}{3}\frac{1}{3}\frac{1}{3}$; $\frac{1}{3}\frac{2}{3}\frac{2}{3}$): (i) x, y, z; (ii) $-y, x-y, z$; (iii) $y-x, -x, z$; (iv) $-x, -y, -z$; (v) $y, y-x, -z$; (vi) $x-y, x, -z$.

	(1)	(2)	Operation	Centring	Translation
C(5)—N(6)	1.322 (2)	1.323 (3)	i	1	0 0 0
C(5)—C(5)	1.380 (3)	1.371 (4)	ii	1	0 0 0
C(5)—C(5)	1.380 (2)	1.371 (2)	iii	1	0 0 0
N(6)—C(5)	1.322 (2)	1.323 (3)	i	1	0 0 0
N(6)—C(8)	1.446 (4)	1.467 (5)	i	1	0 −1 0
N(6)—C(7)	1.450 (2)	1.456 (3)	i	1	0 0 0
M(1)—Cl(3)	2.3431 (7)	2.3436 (8)	i	1	0 0 0
M(2)—Cl(4)	2.3280 (8)	2.330 (1)	i	1	0 0 0
C(8)—N(6)—C(5)	119.1 (1)	119.6 (1)			
C(7)—N(6)—C(5)	120.16 (7)	119.78 (9)			
C(7)—N(6)—C(8)	118.7 (1)	119.0 (1)			
C(5)—C(5)—N(6)	149.4 (2)	149.2 (3)			
C(5)—C(5)—N(6)	150.6 (2)	150.8 (3)			
C(5)—C(5)—C(5)	60.00 (7)	60.0 (1)			
Cl(3)—*M*(1)—Cl(3)	89.823 (2)	89.889 (3)			
Cl(4)—*M*(2)—Cl(4)	90.113 (2)	90.085 (2)			

Discussion. Atomic coordinates and anisotropic displacement parameters are given in Table 1, distances and angles are given in Table 2. The cell is shown in Fig. 1. The structure contains two types of MCl_6^- (M = Nb,Ta) octahedra, different with respect to crystallographic equivalence. This behavior is the reason

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* Lists of structure factors, anisotropic thermal parameters bond distances and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54741 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

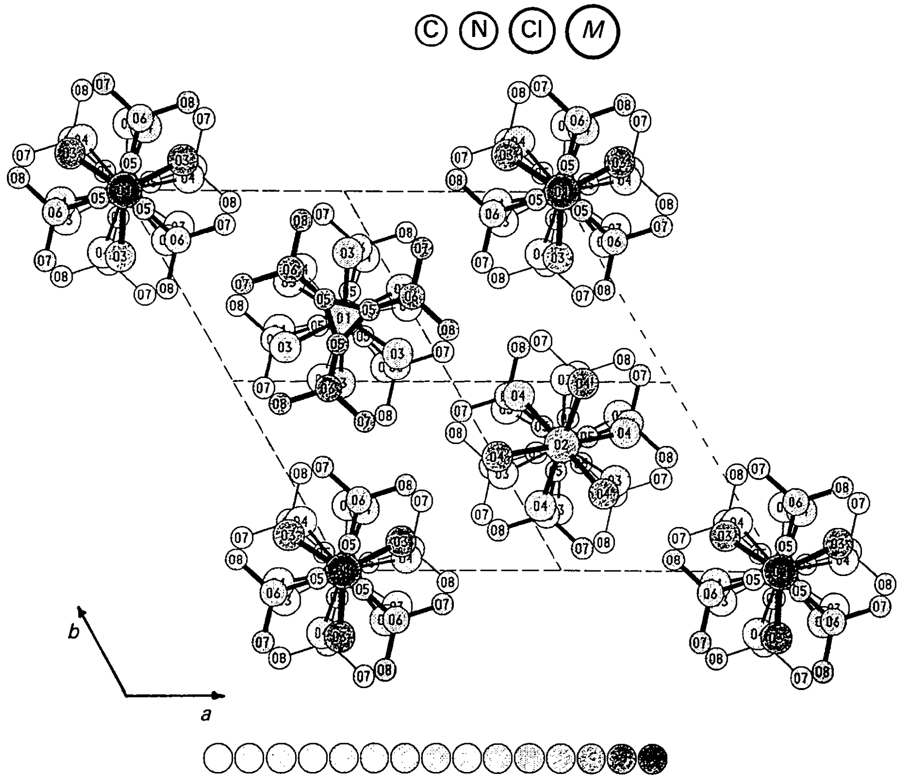

Fig. 1. Projection of the cell. The numbering scheme refers to the labels of atoms in Table 1. The grade of shading indicates different heights (− 10.0 to 10.0 Å) of the atoms with respect to the drawing plane.

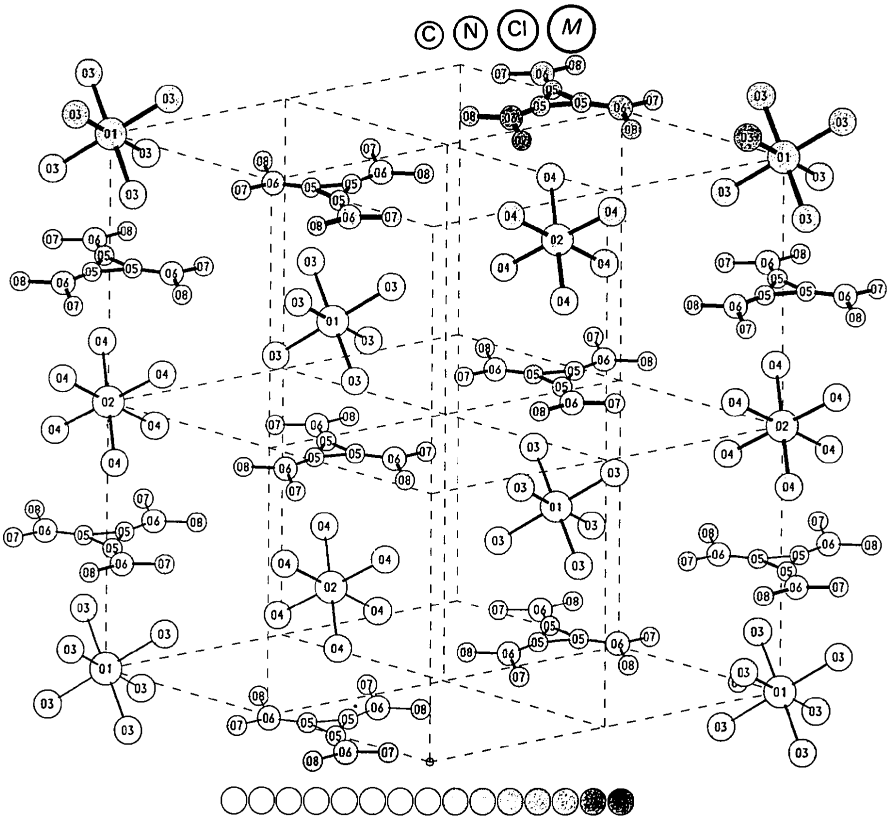

Fig. 2. Packing diagram. Octahedron (I) is defined as *M*(2)Cl(4) and octahedron (II) is defined as *M*(1)Cl(3). The grade of shading indicates different heights (−8.0 to 8.0 Å) of the atoms with respect to the drawing plane.

for the different orientation of the cation with respect to the Cl atoms. The Cl triangle of octahedron (I) [Cl(4)] close to the cation has nearly the same orientation as the N triangle of the cation, while the related triangle of octahedron (II) [Cl(3)] is twisted by 60° (Fig. 2). This arrangement may be the reason for charge-transfer contacts and the observed properties of colour and stability. A more accurate investigation with respect to electron density distributions has been started. Compounds containing the $\mathrm{NbCl_6^-}$ or the $\mathrm{TaCl_6^-}$ ion such as the K salt are colourless solids. The $[\mathrm{C_3\{N(CH_3)_2\}_3}]^+.\mathrm{ClO_4^-}$ (Ku & Sundaralingam, 1972) is also colourless. So the intense blue colour of compound (1) and the intense red colour of compound (2) can be attributed to an interionic outer-sphere charge-transfer transition. This conclusion is supported by the observation that the colour vanishes in solution and by the value of the Cl—N distance of 3.59 Å, which is in the typical range for interionic charge-transfer salts. A detailed publication with respect to the theoretical approach to the effect is in preparation.

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References

*ATARI CRYSTAN*88 (1989). Proc. CIC Meet., Tübingen, Germany. Berlin: Springer-Verlag.

Flack, H. D. (1975). *J. Appl. Cryst.* **8**, 520–522.

Ku, A. T. & Sundaralingam, M. (1972). *J. Am. Chem. Soc.* **94**, 1688–1700.

Weiss, R. (1979). *Tetrahedron Lett.* **40**, 3295–3296.

Weiss, R. & Schloter, K. (1975). *Tetrahedron Lett.* **35**, 3491–3493.

Yoshida, Z. & Tawara, Y. (1971). *J. Am. Chem. Soc.* **92**, 2573–2578.

Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 421–424.

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Structures of Methyl- and Benzyl(η^1-azaferrocene)cobaloximes

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Abstract. (I) (η^1-Azaferrocene-*N*)bis(dimethylglyoximato-*N*,*N'*)(methyl)cobalt(III), $[\mathrm{Co(FeC_9H_9N)(C_4H_7N_2O_2)_2(CH_3)}]$, $M_r = 491.22$, monoclinic, $P2_1/c$, $a = 8.539\,(3)$, $b = 17.957\,(7)$, $c = 14.215\,(6)$ Å, $\beta = 102.54\,(4)°$, $V = 2127.7$ Å^3, $Z = 4$, $D_x = 1.533$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71073$ Å, $\mu = 14.64$ cm^{-1}, $F(000) = 1004$, room temperature, final $R = 0.039$, $wR = 0.040$ for 2948 observed reflections. (II) (η^1-Azaferrocene-*N*)benzylbis(dimethylglyoximato-*N*,*N'*)cobalt(III), $[\mathrm{Co(FeC_9H_9N)(C_4H_7N_2O_2)_2(C_7H_7)}]$, $M_r = 567.31$, triclinic, $P\bar{1}$, $a = 10.619\,(4)$, $b = 11.353\,(4)$, $c = 12.693\,(5)$ Å, $\alpha = 85.43\,(4)$, $\beta = 119.48\,(5)$, $\gamma = 109.07\,(4)°$, $V = 1252.87$ Å^3, $Z = 2$, $D_x = 1.503$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71073$ Å, $\mu = 12.49$ cm^{-1}, $F(000) = 588$, room temperature, final $R = 0.049$, $wR = 0.056$ for 2285 observed reflections. This work presents X-ray structures of two binuclear cobaloximes, containing axially coordinated azaferrocene. Co—N(ax.) and Co—C bond lengths are discussed and compared with those of other analogs. The structural *trans* effect of (I) and (II) is analyzed in terms of σ-donor power and π-acceptor properties of azaferrocene.

Introduction. The structural and reaction chemistry of alkylcobaloximes attracts great interest since these complexes are considered as models for coenzyme $\mathrm{B_{12}}$ (Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985; Randaccio, Bresciani Pahor, Zangrando & Marzilli, 1989; Bresciani Pahor, Geremia, Lopez, Randaccio & Zangrando, 1990) and set up useful sources of alkyl radicals *via* Co—C bond homolysis (Pattenden, 1988; Giese, Hartung, He, Hüter & Koch, 1989). Recently, binuclear alkylcobaloximes containing azaferrocene (AF) [(η^5-2,4-cyclopentadien-1-yl)(η^5-1*H*-pyrrol-1-yl)iron] as axial ligand have been synthesized (Zakrzewski & Giannotti, 1990), confirming that the σ–π bridging is a common feature of heterocyclic ligands (Mathey, 1987; Zakrzewski, 1990). The crystal structures of the two alkyl(η^1-azaferrocene)cobaloximes (I) and (II) were determined in order to provide a better understanding of N-ligating properties of AF. This

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