Discussion. The refined atomic coordinates and equivalent isotropic displacement parameters are given in Table 1* with selected bond distances and angles in Table 2. The molecular structures of the two types of ions present in the asymmetric unit are presented in Fig. 1. The three-dimensional packing diagram is shown in Fig. 2

The binuclear tungsten molecule exhibits the expected confacial bioctahedral geometry with three bridging chlorides and three terminal chlorides per metal atom which are staggered with respect to the bridging atoms. The phosphonium cations adopt the characteristic triarylphosphine propeller arrangement of the aromatic rings.

The $[W_2Cl_9]^{3-}$ dimeric unit has been synthesized previously in the form of the Cs^+ (Lewis, Nyholm & Smith, 1969) and n-Bu_4N^+ (Ziegler & Risen, 1972) salts, and has been structurally characterized with a K^+ counterion (Watson & Waser, 1958). The earlier value of 2·409 Å for the W—W bond distance in the potassium salt does not differ significantly from the value of 2·4329 (6) Å for the corresponding distance in the present structure with a large phosphonium cation. The rigidity of the M—M bond in the tungsten system is in direct contrast to the extreme flexibility of the dimetal unit in the molybdenum analogue. Single-crystal studies of $Mo_2Cl_9^{3-}$ with various counterions have given values from 2·610 (2)

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* Full lists of bond lengths and · angles, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53229 (93 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

to 2·815 (3) Å for the Mo—Mo bond separation (Subbotin & Aslanov, 1986a; Saillant, Jackson, Streib, Folting & Wentworth, 1971; Stranger, Smith & Grey, 1989; Subbotin & Aslanov, 1986b). The present study demonstrates the increased tendency for the third-row transition elements to form strong metal–metal interactions.

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Bis(N-piperidyldithiocarbamato)copper(III) Hexafluorophosphate: an Unexpected Product from the Disproportionation of 1,12-Bis(N-piperidyl)-2,5,8,11-tetrathiadodeca-1,12-dithionato-Cu^I.PF$_6$

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Abstract. $[Cu(C_6H_{10}NS_2)_2]^+.PF_6^-$, $M_r = 529\cdot1$, monoclinic, $P2_1/c$, $a = 7\cdot816$ (2), $b = 18\cdot428$ (2), $c = 13\cdot883$ (2) Å, $\beta = 94\cdot94$ (2)°, $V = 1992$ Å^3, $Z = 4$, $D_x = 1\cdot764$ g cm^{-3}, λ(Mo Kα) = 0·71069 Å, $\mu = 16\cdot34$ cm^{-1}, $F(000) = 1072$, $T = 297$ (1) K, final $R = 0\cdot039$ for 2508 observed reflections. The crystal contains two crystallographically independent bis(N-piperidyldithiocarbamato)copper(III) cations, each of which has its Cu atom at a centre of symmetry. Cations stack with a Cu···Cu separation of only

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3·908 Å. Each Cu atom is pseudo-octahedrally coordinated with four Cu^{III}—S bond lengths ranging from 2·206 (2) to 2·222 (2) Å and two weaker Cu^{III}···S bonds [3·102 (2) and 3·199 (2) Å], the latter linking the cations in polymeric chains parallel to **a**. The PF_6^- ions are regular octahedra displaying slight orientational disorder.

Introduction. We have recently prepared an air stable Cu^I complex of a novel, potentially hexadentate sulfur podand, 1,12-bis(N-piperidyl)-2,5,8,11-tetrathiadodeca-1,12-dithione (Koch & Sacht, 1989). This complex has been found to be unstable in acetone solution, undergoing an unexpected disproportionation, to yield *inter alia* the title compound bis(N-piperidyldithiocarbamato)copper(III) hexafluorophosphate $[Cu(pipdtc)_2]PF_6$. This disproportionation is unusual in that a two-electron oxidation of the Cu^I occurs in the absence of powerful oxidants. While other Cu^{III} dithiocarbamate complexes are well documented (Coucouvanis, 1979), these complexes are usually prepared by means of oxidation of the corresponding Cu^{II} complexes (Golding, Harris, Jessop & Tennant, 1972). In our case preliminary experiments suggest that the oxidation may be photochemically induced.

In view of the paucity of structural details of Cu^{III} dithiocarbamate complexes, we here report the crystal and molecular structure of $[Cu(pipdtc)_2]PF_6$, the crystals of which were obtained as described above.

Experimental. Suitable black crystals with a metallic lustre of the title compound were obtained on leaving a solution of $[Cu(C_{18}H_{32}N_2S_6)]PF_6$ in acetone-d_6 for several days. Crystal size 0·19 × 0·25 × 0·28 mm. Data collected on an Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions from least-squares refinement of 24 reflections in range $16 < \theta < 17°$; ω–2θ scan, ω scan width varied as $(0·95 + 0·35\tan\theta)°$, aperture width as $(1·12 + 1·05\tan\theta)$ mm; max. scan time 40 s; h,k,l ranges $-9 \le h \le 9$, $0 \le k \le 21$, $0 \le l \le 16$; $(\sin\theta/\lambda)_{max} = 0·6$ Å^{-1}. Intensity control reflections ($\overline{6}42$, 1,13,4, $\overline{3}$,2,10) monitored every 60 min showed intensity decay < 1%. 3790 reflections measured, 64 systematic absences, 3134 unique ($R_{int} = 0·019$), 2508 observed reflections, $I > 3\sigma(I)$. Lp corrections and empirical absorption corrections based on 9 reflections with $\chi \simeq 90°$ using program EAC of the Enraf–Nonius package (Enraf–Nonius, 1979), min. and max. absorption correction factors 0·9384, 0·9996. Structure solved by Patterson and difference Fourier methods and refined by full-matrix least squares ($SHELX76$, Sheldrick, 1976). Final values $R = 0·039$, $wR = 0·044$ with $w = [\sigma^2(F_o) + 5·22 \times 10^{-4}F_o^2]^{-1}$ which gave a satisfactory analysis of variance; $S = 2·026$. Final $(\Delta/\sigma)_{max} = 0·31$, $(\Delta/\sigma)_{av} = 0·024$ for 240

Table 1. *Final fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for non-H atoms*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu(1)	5000	5000	5000	33 (0)
S(1)	3343 (2)	5886 (1)	5469 (1)	34 (0)
S(2)	5309 (2)	5827 (1)	3879 (1)	36 (0)
N(1)	3354 (5)	6988 (2)	4183 (3)	34 (1)
C(1)	3893 (5)	6349 (3)	4458 (3)	31 (1)
C(2)	4091 (7)	7379 (3)	3385 (4)	46 (2)
C(3)	2723 (7)	7656 (3)	2668 (4)	55 (2)
C(4)	1371 (8)	8093 (3)	3140 (4)	55 (2)
C(5)	635 (7)	7650 (3)	3925 (4)	52 (2)
C(6)	2026 (7)	7383 (3)	4666 (4)	46 (2)
Cu(2)	0	5000	5000	35 (0)
S(3)	537 (2)	4526 (1)	6455 (1)	39 (0)
S(4)	−1498 (2)	5731 (1)	5884 (1)	36 (0)
N(2)	−1258 (5)	5243 (2)	7719 (3)	40 (1)
C(7)	−825 (6)	5183 (2)	6838 (3)	32 (1)
C(8)	−2545 (7)	5769 (3)	8005 (4)	48 (2)
C(9)	−4014 (7)	5359 (4)	8384 (5)	60 (2)
C(10)	−3424 (9)	4837 (3)	9183 (5)	69 (3)
C(11)	−2047 (9)	4333 (3)	8863 (5)	68 (3)
C(12)	−590 (7)	4751 (3)	8504 (4)	52 (2)
P	2825 (2)	2972 (1)	8923 (1)	46 (0)
F(1)	4809 (6)	3080 (4)	9029 (5)	147 (3)
F(2)	864 (6)	2853 (4)	8784 (4)	140 (3)
F(3)	2863 (7)	2383 (3)	9747 (4)	113 (2)
F(4)	2813 (8)	3552 (3)	8121 (4)	140 (3)
F(5)	2569 (10)	3558 (3)	9684 (4)	159 (4)
F(6)	3093 (9)	2356 (3)	8172 (5)	150 (3)

parameters. $\Delta\rho$ excursions 0·70, $-0·45$ e Å^{-3}, maxima in vicinity of PF_6^- ion. All non-H atoms anisotropic. H atoms located in difference Fourier syntheses and included in idealized positions (C—H = 1·08 Å) with fixed U_{iso} values of 0·071 (6) and 0·082 (7) Å^2 for the two independent piperidine rings respectively. Atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Program $PARST$ (Nardelli, 1983) used for geometrical calculations and $PLUTO$ (Motherwell, 1989) for illustrations.

Discussion. Final fractional coordinates and U_{eq} for non-H atoms are listed in Table 1.* Fig. 1 shows the atomic numbering for the cations and Fig. 2 illustrates the packing.

The compound consists of the ionic units $Cu(pipdtc)_2^+$ and PF_6^-. Two crystallographically independent cations have their Cu atoms at Wyckoff positions (a) and (b) with site symmetry $\bar{1}$, requiring strictly planar coordination of each Cu atom by four S atoms. Pseudo-octahedral coordination of each

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes, torsion angles, intermolecular contacts and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53312 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$[Cu(C_6H_{10}NS_2)_2]^+ .PF_6^-$

metal atom results from weakly bonded S atoms of adjacent cations at unique Cu···S distances of 3·102 (2) and 3·199 (2) Å. The arrangement is similar to that found in bis(*N,N*-dimethyldithiocarbamato)-copper(II) (Einstein & Field, 1974) where Cu···S is 3·159 Å. With a formal oxidation state of +3 for Cu, the Cu^{III}—S bond lengths (Table 2) are in the range 2·206 (2) to 2·222 (2) Å, which compares favourably with an average value of 2·22 (2) Å reported for bis(*N,N*-di-*n*-butyldithiocarbamato)-copper(III) triiodide (Wijnhoven, Van den Hark & Beurskens, 1972) and with a range of 2·203 (3) to 2·216 (4) Å observed in the closely related bis-(*N*-pyrrolidyldithiocarbamato)copper(III) cation

Table 2. *Bond distances* (Å) *and bond angles* (°) *for the two independent* Cu(pipdtc)$_2^+$ *cations*

Cu(1)—S(1)	2·216 (2)	Cu(2)—S(3)	2·208 (2)
Cu(1)—S(2)	2·206 (2)	Cu(2)—S(4)	2·222 (2)
S(1)—C(1)	1·728 (5)	S(3)—C(7)	1·726 (5)
S(2)—C(1)	1·717 (5)	S(4)—C(7)	1·712 (4)
C(1)—N(1)	1·297 (7)	C(7)—N(2)	1·302 (6)
N(1)—C(2)	1·479 (7)	N(2)—C(8)	1·476 (7)
C(2)—C(3)	1·487 (8)	C(8)—C(9)	1·507 (9)
C(3)—C(4)	1·521 (8)	C(9)—C(10)	1·510 (9)
C(4)—C(5)	1·514 (8)	C(10)—C(11)	1·517 (9)
C(5)—C(6)	1·513 (8)	C(11)—C(12)	1·495 (9)
C(6)—N(1)	1·475 (7)	C(12)—N(12)	1·478 (7)
Cu(1)—S(4^i)	3·199 (2)	Cu(2)—S(1)	3·102 (2)

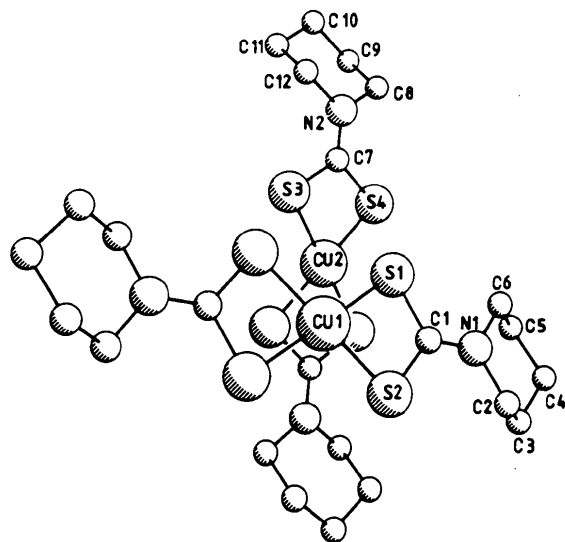| S(1)—Cu(1)—S(2)	78·5 (1)	S(3)—Cu(2)—S(4)	78·6 (1)
Cu(1)—S(1)—C(1)	86·1 (2)	Cu(2)—S(3)—C(7)	86·0 (2)
Cu(1)—S(2)—C(1)	86·7 (2)	Cu(2)—S(4)—C(7)	85·9 (2)
S(1)—C(1)—S(2)	108·6 (3)	S(3)—C(7)—S(4)	109·4 (2)
S(1)—C(1)—N(1)	126·2 (4)	S(3)—C(7)—N(2)	124·5 (3)
S(2)—C(1)—N(1)	125·2 (3)	S(4)—C(7)—N(2)	126·1 (3)
C(1)—N(1)—C(2)	121·7 (4)	C(7)—N(2)—C(8)	123·2 (4)
C(1)—N(1)—C(6)	122·5 (4)	C(7)—N(2)—C(12)	122·5 (4)
C(2)—N(1)—C(6)	115·8 (4)	C(8)—N(2)—C(12)	114·2 (4)
N(1)—C(2)—C(3)	111·4 (5)	N(2)—C(8)—C(9)	108·8 (5)
C(2)—C(3)—C(4)	112·3 (5)	C(8)—C(9)—C(10)	112·5 (5)
C(3)—C(4)—C(5)	110·2 (5)	C(9)—C(10)—C(11)	110·8 (5)
C(4)—C(5)—C(6)	111·7 (5)	C(10)—C(11)—C(12)	111·2 (5)
C(5)—C(6)—N(1)	110·1 (4)	C(11)—C(12)—N(2)	109·3 (5)

Symmetry code: (i) $1 + x, y, z$.

Fig. 1. Perspective view of the two independent Cu(pipdtc)$_2^+$ cations including atom numbering. (H atoms omitted for clarity.)
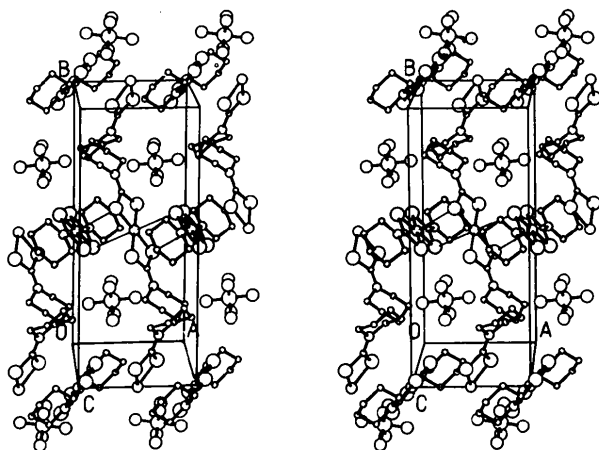

Fig. 2. Stereoscopic packing diagram viewed approximately parallel to the *c* axis. Representative weak Cu···S bonds are indicated by single lines.

(Brown, 1979). There is a systematic asymmetry in the Cu^{III}—S distances in the present case; in one cation the unique Cu^{III}—S distances differ by 3·5σ and in the other by 5σ. The longer pair involves atoms S(1) and S(4) which engage in the weak Cu···S bonds linking the cations. The four S—C distances are equivalent and average 1·721 (8) Å while the S—C—S 'bite' angles are consistent with the average of 111° reported for symmetrically bonded dtc ligands (Wijnhoven *et al.*, 1972). Atoms N(1) and N(2) deviate by 0·017 (4) and 0·031 (4) Å from the planes formed by their respective bonded C atoms. A least-squares plane calculation including atoms S(1), S(2), C(1), N(1), C(2) and C(6) shows that the first four atoms are coplanar to within about 0·01 Å while atoms C(2) and C(6) deviate by −0·155 (6) and 0·127 (6) Å respectively. The same fragment in the second cation has a higher degree of planarity, the maximum deviation of 0·084 (6) Å being that of atom C(8).

The weak Cu···S bonds link cations in a linear polymeric arrangement along the *x* direction (Fig. 2). Alternating CuS$_4$ coordination planes (*e.g.* those centred at $0, \frac{1}{2}, \frac{1}{2}$, and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) are tilted at 26·0 (1)° to each other and the Cu···Cu distance is 3·908 Å (*a*/2). The latter distance is close to the value of 4·043 Å observed in bis(*N,N*-dimethyldithiocarbamato)-copper(II) which has an analogous polymeric structure, but considerably shorter than that observed in bis(*N,N*-di-*n*-butyldithiocarbamato)copper(III) triiodide, 4·31 Å. In the latter structure, Cu atoms occupy Wyckoff positions (*a*) and (*c*) of the same

space group as the present case and the shortest Cu···S distance is 3·34 (2) Å.

The PF_6^- ion has regular octahedral geometry with an average P—F distance of 1·55 (2) Å. Uniformly large U_{eq} parameters for the F atoms (Table 1) and the presence of large residual peaks (up to 0·70 e Å^{-3}) in their vicinity indicated possible minor anion disorder. An alternative orientation for the PF_6^- ion was not readily apparent and no attempt was made to model disorder.

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cis-Dichloro[(*N*,*N*-diéthyldithiocarbamoyl)-6 désoxy-6 (di-*O*-isopropylidène)-1,2:3,4 α-D-galactopyrannose]platine(II)–Acétone

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Abstract. [PtCl$_2$(C$_{17}$H$_{29}$NO$_5$S$_2$)].C$_3$H$_6$O, M_r = 715·6, orthorhombic, $P2_12_12_1$, a = 10·594 (2), b = 14·099 (2), c = 18·433 (3) Å, V = 2753 (1) Å^3, Z = 4, D_x = 1·73 Mg m^{-3}, λ(Mo K$\bar{\alpha}$) = 0·7107 Å, μ = 5·52 mm^{-1}, $F(000)$ = 1416, T = 295 (1) K, R = 0·034 for 2576 independent observed reflections. The Pt atom displays square-planar coordination. It is linked to two Cl and two S atoms. Apart from the terminal C atoms of the *N*,*N*-diethyl substituents, the dichloro(*N*,*N*-diethyldithiocarbamoyl)platinum group is approximately planar. One of the two five-membered rings is in an envelope form and the other is intermediate between an envelope and a half-chair form. The pyranosyl ring has a skew-boat conformation. In the dithiocarbamoyl group, the shortest C—S and C—N distances, 1·69 (1) and 1·28 (1) Å, respectively, are due to a delocalized orbital. All other bond lengths agree with values published for similar compounds.

Introduction. La résolution de la structure cristalline du *cis*-dichloro[(*N*,*N*-diéthyldithiocarbamoyl)-6

désoxy-6 (di-*O*-isopropylidène)-1,2:3,4 α-D-galacto-pyrannose]platine(II)–acétone a été entreprise dans le cadre de la synthèse et de l'étude des composés de coordination du platine(II). Le produit utilisé a été préparé à la température ambiante par addition, à l'abri de la lumière, d'une solution aqueuse de K$_2$PtCl$_4$ à une solution éthanolique de désoxy-6 (*N*,*N*-diéthyldithiocarbamoyl)-6 (di-*O*-isopropylidène)-1,2:3,4 α-D-galactopyrannose. Les deux réactifs sont pris en quantités équimoléculaires. Au bout de quelques jours, il se forme un précipité qui est mis en solution dans le chloroforme. On déshydrate par addition de Na$_2$SO$_4$, évapore à sec et sépare le complexe en le dissolvant dans l'acétone. Des cristaux ont été obtenus par évaporation lente de la solution acétonique.

Partie expérimentale. Cristal parallélépipédique : 0,15 × 0,22 × 0,32 mm. Dimensions de la maille déterminées sur monocristal avec 25 réflexions telles que 7,29 ≤ θ ≤ 15,47°. Diffractomètre Enraf–Nonius CAD-4. Balayage θ/2θ d'amplitude $s(°)$ = 0,85 +