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Metal Complexes of Sulfur–Nitrogen Ligands: the Structure of Amino(triphenyl)phosphonium [Di(thiazane)-3-eno](thiosulfato)(triphenylphosphine)platinate

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Abstract. $[P(C_6H_5)_3(NH_2)][Pt(S_2N_2H)(S_2O_3)(C_{18}H_{15}P)]$, $M_r = 940{\cdot}96$, monoclinic, $P2_1/n$, $a = 12{\cdot}222\,(4)$, $b = 17{\cdot}155\,(4)$, $c = 18{\cdot}126\,(5)$ Å, $\beta = 100{\cdot}63\,(2)°$, $V = 3735\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}674$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 39{\cdot}18$ cm^{-1}, $F(000) = 1864$, $T = 298$ K, $R = 0{\cdot}0444$ for 3015 observed reflections. The Pt atom is in a square-planar environment, coordinated to S and N atoms of the chelating S_2N_2H ligand, a thiosulfate S atom *trans* to S and triphenylphosphine. There are H-bonding interactions between the S_2O_3 ligand, the S_2N_2H hydrogen and the amine hydrogens of the $Ph_3PNH_2^+$ cation.

Introduction. A number of metal–sulfur–nitrogen complexes are known (Kelly & Woollins, 1986) but, to date, there are no structurally characterized examples of mixed-ligand complexes containing S_2N_2H– and phosphine ligands. Compounds of this type may be of use as sulfur–nitrogen reagents in syntheses.

Experimental. The compound (1) was prepared by reaction of S_4N_4 with $Pt(PPh_3)_3$ in air, the crystals being obtained from THF/petroleum ether (Kelly, 1987). Crystal size $0{\cdot}20 \times 0{\cdot}15 \times 0{\cdot}25$ mm. Data collected on Enraf–Nonius CAD-4 diffractometer, lattice parameters from 25 reflections, $24 < 2\theta < 26°$. Total of 4705 reflections measured using $\omega/2\theta$ scan mode, $3 < 2\theta < 44°$, in the range h: 0→12, k: 0→18, l: −19→19. Intensities of three standard reflections (162, 081, $\bar{1}6\bar{2}$) measured every 1 h showed no decay during data collection, orientation standards checked every 100 reflections. Corrections for Lorentz, polarization and absorption (North, Phillips & Mathews, 1968) applied; max. and min. relative transmission factors 99·9 and 83·6%. 4520 unique reflections with 1505 considered unobserved $[I < 3\sigma(I)]$, systematic absences $h0l$, $h + l = 2n$ and $0k0$, $k = 2n + 1$ uniquely indicate $P2_1/n$. Position of Pt atom located from Patterson synthesis and all non-H atoms found from successive Fourier difference syntheses. Anisotropic displacement factor coefficients for all non-H atoms, phenyl rings refined as rigid group with refined group $U_{\rm iso}$ values for hydrogens. Other hydrogens refined freely with isotropic coefficients. Final refinement on F by full-matrix least-squares methods. Largest peak in final difference Fourier map $0{\cdot}97$ e Å^{-3} close to Pt. Weighting scheme $w = 1/(\sigma^2F + gF^2)$ where $g = 0{\cdot}0001$ applied. Max. Δ/σ in final cycle 0·08. Final $R = 0{\cdot}0444$, $wR = 0{\cdot}0389$. Computing with *SHELX*80 (Sheldrick, 1980) on

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors*

	x	*y*	*z*	*U*(Å$^2 \times 10^3$)*
Pt(1)	1037·2 (4)	300·7 (3)	2955·7 (2)	37·2 (2)
S(3)	1718 (3)	1290 (2)	3815 (2)	45 (1)
S(4)	1959 (2)	829 (2)	4881 (2)	41 (1)
O(100)	848 (6)	625 (4)	5034 (4)	48 (3)
O(101)	2462 (6)	1448 (5)	5359 (4)	58 (3)
O(102)	2638 (6)	136 (5)	4905 (4)	56 (3)
S(1)	134 (3)	−513 (2)	2069 (2)	55 (1)
N(1)	−819 (8)	−961 (6)	2480 (5)	66 (5)
S(2)	−872 (3)	−795 (2)	3309 (2)	60 (1)
N(2)	30 (7)	−153 (6)	3613 (5)	45 (4)
P(1)	2283 (2)	676 (2)	2261 (2)	39 (1)
C(11)	1503 (6)	2197 (6)	2219 (4)	59 (6)
C(12)	1535 (6)	2995 (6)	2076 (4)	70 (6)
C(13)	2453 (6)	3318 (6)	1831 (4)	75 (6)
C(14)	3339 (6)	2842 (6)	1729 (4)	73 (6)
C(15)	3307 (6)	2044 (6)	1872 (4)	67 (6)
C(10)	2389 (6)	1722 (6)	2117 (4)	48 (5)
C(21)	1495 (6)	755 (5)	713 (5)	57 (5)
C(22)	1235 (6)	438 (5)	−7 (5)	85 (7)
C(23)	1478 (6)	−342 (5)	−127 (5)	96 (8)
C(24)	1983 (6)	−804 (5)	474 (5)	86 (7)
C(25)	2243 (6)	−487 (5)	1194 (5)	66 (6)
C(20)	2000 (6)	292 (5)	1313 (5)	42 (4)
C(31)	4458 (6)	201 (5)	2167 (3)	66 (5)
C(32)	5544 (6)	−30 (5)	2466 (3)	82 (7)
C(33)	5871 (6)	−125 (5)	3240 (3)	78 (7)
C(34)	5113 (6)	10 (5)	3714 (3)	58 (5)
C(35)	4027 (6)	241 (5)	3415 (3)	44 (4)
C(30)	3700 (6)	337 (5)	2641 (3)	42 (4)
P(3)	1925 (3)	−1945 (2)	5841 (2)	47 (1)
N(3)	1489 (9)	−1131 (6)	5483 (6)	60 (5)
C(41)	1899 (8)	−1326 (5)	7228 (6)	80 (7)
C(42)	1840 (8)	−1357 (5)	7988 (6)	106 (9)
C(43)	1705 (8)	−2072 (5)	8327 (6)	91 (8)
C(44)	1629 (8)	−2756 (5)	7905 (6)	95 (8)
C(45)	1688 (8)	−2726 (5)	7145 (6)	89 (8)
C(40)	1823 (8)	−2011 (5)	6806 (6)	50 (5)
C(51)	4115 (7)	−2400 (5)	6289 (4)	63 (6)
C(52)	5215 (7)	−2478 (5)	6192 (4)	83 (7)
C(53)	5533 (7)	−2199 (5)	5540 (4)	61 (6)
C(54)	4750 (7)	−1842 (5)	4985 (4)	76 (7)
C(55)	3649 (7)	−1764 (5)	5082 (4)	67 (6)
C(50)	3332 (7)	−2044 (5)	5734 (4)	41 (5)
C(61)	20 (8)	−2566 (5)	5012 (6)	92 (7)
C(62)	−632 (8)	−3158 (5)	4629 (6)	122 (10)
C(63)	−189 (8)	−3904 (5)	4592 (6)	109 (9)
C(64)	906 (8)	−4057 (5)	4940 (6)	93 (7)
C(65)	1557 (8)	−3465 (5)	5324 (6)	76 (7)
C(60)	1114 (8)	−2719 (5)	5360 (6)	53 (5)

* According to Hamilton (1959).

Table 2. *Selected bond lengths* (Å) *and angles* (°)

S(3)—Pt(1)	2·349 (5)	S(1)—Pt(1)	2·257 (5)
N(2)—Pt(1)	2·020 (10)	P(1)—Pt(1)	2·242 (5)
S(4)—S(3)	2·058 (6)	O(100)—S(4)	1·477 (8)
O(101)—S(4)	1·435 (9)	O(102)—S(4)	1·447 (9)
N(1)—S(1)	1·680 (12)	S(2)—N(1)	1·542 (11)
N(2)—S(2)	1·584 (11)	C(10)—P(1)	1·821 (12)
C(20)—P(1)	1·812 (11)	C(30)—P(1)	1·836 (10)
N(3)—P(3)	1·590 (12)	C(40)—P(3)	1·779 (12)
C(50)—P(3)	1·774 (10)	C(60)—P(3)	1·785 (13)
H(200)—N(2)	0·95 (10)	H(301)—N(3)	0·96 (10)
H(300)—N(3)	0·85 (8)		
S(1)—Pt(1)—S(3)	170·2 (1)	N(2)—Pt(1)—S(3)	93·9 (4)
N(2)—Pt(1)—S(1)	84·9 (4)	P(1)—Pt(1)—S(3)	88·3 (2)
P(1)—Pt(1)—S(1)	94·1 (2)	P(1)—Pt(1)—N(2)	173·1 (3)
S(4)—S(3)—Pt(1)	108·5 (3)	O(100)—S(4)—S(3)	106·9 (4)
O(101)—S(4)—S(3)	104·7 (5)	O(101)—S(4)—O(100)	111·6 (5)
O(102)—S(4)—S(3)	109·0 (4)	O(102)—S(4)—O(100)	110·0 (6)
O(102)—S(4)—O(101)	114·2 (6)	N(1)—S(1)—Pt(1)	104·8 (4)
S(2)—N(1)—S(1)	120·2 (7)	N(2)—S(2)—N(1)	108·5 (6)
S(2)—N(2)—Pt(1)	121·5 (6)	C(10)—P(1)—Pt(1)	115·9 (4)
C(20)—P(1)—Pt(1)	113·4 (4)	C(20)—P(1)—C(10)	103·2 (5)
C(30)—P(1)—Pt(1)	112·9 (3)	C(30)—P(1)—C(10)	106·2 (5)
C(30)—P(1)—C(20)	104·1 (4)	C(11)—C(10)—P(1)	118·7 (3)
C(15)—C(10)—P(1)	121·2 (3)	C(21)—C(20)—P(1)	120·9 (4)
C(25)—C(20)—P(1)	119·1 (4)	C(31)—C(30)—P(1)	120·6 (3)
C(35)—C(30)—P(1)	119·4 (3)	C(40)—P(3)—N(3)	112·2 (6)
C(50)—P(3)—N(3)	107·3 (6)	C(50)—P(3)—C(40)	110·2 (5)
C(60)—P(3)—N(3)	109·9 (6)	C(60)—P(3)—C(40)	107·5 (6)
C(60)—P(3)—C(50)	109·7 (5)	C(41)—C(40)—P(3)	118·4 (4)
C(45)—C(40)—P(3)	121·6 (4)	C(51)—C(50) P(3)	120·9 (3)
C(55)—C(50)—P(3)	119·1 (3)	C(61)—C(60)—P(3)	118·7 (4)
C(65)—C(60)—P(3)	121·3 (4)		
H(200)—N(2)—Pt(1)	120·5 (66)	H(200)—N(2)—S(2)	117·7 (66)
H(301)—N(3)—P(3)	115·8 (61)	H(300)—N(3)—P(3)	125·5 (58)
H(300)—N(3)—H(301)	118·5 (57)		

VAX11/750. Scattering factors from Cromer & Mann (1988). Atomic coordinates are listed in Table 1 and bond distances and angles in Table 2.* A view of the ion pair with the numbering scheme is given in Fig. 1.

Discussion. The crystal structure consists of $[Pt(S_2N_2H)(S_2O_3)(PPh_3)]^-$ anions and $[PPh_3NH_2]^+$ cations. The amino(triphenyl)phosphonium cation is known, its structure having been previously determined as the chloride salt, (2) (Hursthouse, Walker, Warrens & Woollins, 1985). Relative to the chloride salt, the N—P distance in the present structure is shorter [1·590 (12) *vs* 1·615 (6) Å], possibly as a result of stronger H bonding present in the chloride, but all other distances and angles are comparable. H bonding does occur in the present complex, with contacts between H(301) and O(102), H(300) and O(100) (through −*x*, −*y*, 1 − *z*) at 2·01 (9) and 2·17 (8) Å, respectively.

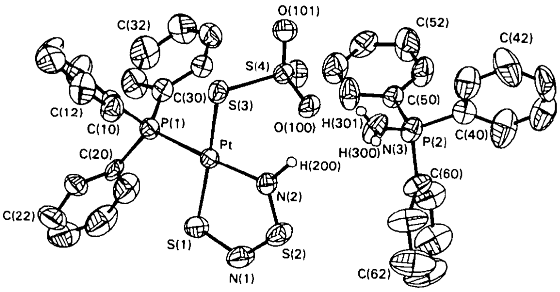

Fig. 1. A diagram of the ion pair $[Pt(S_2N_2H)(S_2O_3)(PPh_3)]$-$[Ph_3PNH_2]$. Hydrogen atoms omitted for clarity.

In the anion the Pt—P distance is slightly shorter than those found in related complexes $[Pt(S_2N_2H)(PMe_3)_2]$ (3), $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ (4) (Jones, Kelly, Warrens, Williams & Woollins, 1986) and $[Pt(S_2N_2)(PPh_3)_2]$ (5) (Jones, Kelly, Williams & Woollins, 1985), 2·263 (1), 2·261 (2) and 2·263 (4) Å, respectively. The Pt—S(1) and Pt—N(2) distances are broadly similar.

The distances within the PtS_2N_2 ring of (1) parallel those of (4) and (5); there are two short and one long N—S bonds. These may be reversed relative to (3) as a result of protonation of the ligand, but limitations in the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51107 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

accuracy of the structure do not allow detailed discussion of this aspect.

The thiosulfate ligand coordinates to Pt *via* S and is H-bonded to the cation *via* the interaction O(100)··· H(200) at 2·04 (8) Å.

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Structure of the 4:3 Complex Between Gadolinium Nitrate and 18-Crown-6 Ether: $[Gd(NO_3)_2(C_{12}H_{24}O_6)]_3[Gd(NO_3)_6]$*

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Abstract. Tris[dinitrato(1,4,7,10,13,16-hexaoxacyclooctadecane)gadolinium(III)] hexanitratogadolinate(III), M_r = 2166·02, monoclinic, $C2$, a = 28·640 (4), b = 11·087 (2), c = 11·993 (2) Å, β = 112·40 (1)°, V = 3521 (1) Å^3, Z = 2, D_m = 2·01 (by flotation in CCl_4/CH_2Br_2), D_x = 2·04 g cm^{-3}, graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·71073 Å), μ(Mo $K\alpha$) = 38·57 cm^{-1}, F(000) = 2120, $\mu r \simeq$ 0·80, transmission range 0·19–0·29, T = 295 K, R = 0·049 for 4361 unique reflections. The complex contains a $[Gd(NO_3)_6]^{3-}$ anion with symmetry 2 (C_2) and two types of $[Gd(NO_3)_2(\text{18-crown-6})]^+$ cations, one in special position with symmetry 2 and the other in a general position, in the ratio 1:1:2, respectively. The polar crystal packing is pseudo-centrosymmetric and the ions with the crystallographic symmetry 2 exhibit approximate $2/m$ (C_{2h}) symmetry. This property is the cause of very strong correlation parameters between atoms related by the pseudo-mirror plane and complicates the refinement. The cation located on a general position is well defined and displays interesting differences with respect to the analogous ion with the metal at the origin. The explanation is given by a conformational analysis on the six-membered ring arrangement of the O(ether) atoms around Gd. The mean Gd—O_{eth} and Gd—O_{nit} distances are respectively 2·55 (2) and 2·46 (1) Å in the crown complexes, while in the hexanitrate the Gd—O average bond length is 2·57 (1) Å.

Introduction. The guest–host complexes obtained by reacting lanthanide ions with synthetic ionophores have several potential applications (Bünzli, 1987). In our laboratory, special attention is given to the relationship between the crystal and molecular structure of these complexes and their luminescent properties (*cf.* Nicolò, Plancherel, Bünzli & Chapuis, 1987; Plancherel, Jin, Massara & Bünzli, 1987).

Following the structure determination of the 4:3 complex between $Nd(NO_3)_3$ and 18C6 (18-crown-6 ether: 1,4,7,10,13,16-hexaoxacyclooctadecane) (Bünzli, Klein, Wessner, Schenk, Chapuis, Bombieri & De Paoli, 1981), we have undertaken a detailed photophysical study of the corresponding Eu- and Eu-doped Gd complexes (Bünzli & Pradervand, 1986). This investigation revealed that the two compounds are isostructural and contain $[Ln(NO_3)_6]^{3-}$ anions with an inversion centre and two types of $[Ln(NO_3)_2(18C6)]^+$ cations with approximate symmetry $2mm$ (C_{2v}), in the ratio 1:1:2. The structure of the Eu complex was solved

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