Sulphamato-complexes of the Platinum Metals

By **W. P. Griffith** and **D. Pawson**, Department of Chemistry, Imperial College, London SW7 2AY

The new complexes $K_3[M(NH_2SO_3)Cl_5]$ (M = Rh, Ir, Ru, or Os) and $K_2[Pd(NH_2SO_3)_2Cl_2]$ have been characterised and their chemical reactions studied. Spectroscopic data suggest that sulphamate is nitrogen-bonded to the metal in these salts, in $K_2[Pt(NH_2SO_3)_2X_2]$ and in the imido-sulphonate $Cs_4[Pt(NHSO_3)_2Cl_2]$.

WE have recently described the properties and structure of the nitrido-bridged species $K_3[Ru_2NCl_8(H_2O)_2]$,[1] first made [2] by reduction of $K_2[Ru(NO)Cl_5]$. Another recent publication has shown that $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$ can be made from ruthenium trichloride and sulphamic acid in the presence of chloride ion.[3] As part of a general study of platinum metal nitrido-complexes we have studied the reaction between the metal halogeno-complexes and sulphamate ion in order to establish the nature of the intermediate species involved, and to investigate the possibility of making nitrido-complexes from them. There are few fully characterised sulphamato-complexes in the literature: those previously reported are of platinum(II) [4,5] and $[M(NH_2SO_3)(NH_3)_5]^{2+}$ (M = Co [6,7] and Ru [8]).

I.r. spectra of sulphamate derivatives in the N–H and N–S regions (cm^{-1})

	$\nu_{NH_n}^{as}$	$\nu_{NH_n}^{s}$	$\delta_{NH_n}^{as}$	$\delta_{NH_n}^{s}$	NH_nrock	ν_{S-N}
$K(NH_2SO_3)$ [a]	3328s	3250s	1546m	1128m	956m	805vs
$K(ND_2SO_3)$	2508s	2417s	1160m	803m	718m	712vs
$K_3[Rh(NH_2SO_3)Cl_5]$	3248m	3143m	1516m	1151m	676w	724vs
$K_3[Rh(ND_2SO_3)Cl_5]$	2424m	2315m	1122m	903m	516w	708vs
$K_3[RhCl_6],1{\cdot}1NH_3SO_3$	3075s	2990vs	1550s	1389m	999m	692s
$K_3[RhCl_6],1{\cdot}1ND_3SO_3$	2279s	2210s	1124s	1071m	791m	678s
NH_3SO_3 [b]	3200s	3140s	1570m	1446m	1015m	695s
ND_3SO_3	2370s	2299s	1143m	1102m	801m	683s
$Cs_4[Pt(NHSO_3)_2Cl_2]$	3244s				1270m	883s
$Cs_4[Pt(NDSO_3)_2Cl_2]$	2401s				960m	839s

[a] Using the assignments of L. Kaityar, *Indian J. Pure Appl. Phys.*, 1968, **6**, 686. [b] Using the assignments of A. M. Vaugnat and B. L. Wagner, *J. Chem. Phys.*, 1957, **26**, 77.

We find that reaction of hexachloro-complexes of trivalent rhodium, iridium, ruthenium, and osmium with sulphamic acid in the presence of potassium chloride yields $K_3[M(NH_2SO_3)Cl_5]$ in good yield, and a similar method with $K_2[PdCl_4]$ gives $K_2[Pd(NH_2SO_3)_2Cl_2]$. The magnetic moments of the four pentachloro-species indicate that the metal is in the trivalent state, and, in the case of the rhodium complex, *X*-ray powder photographs show that the complex contains no free $K_3[RhCl_6]$, potassium sulphamate or sulphamic acid.

Several properties suggest that the sulphamato-ligand is bonded to the metal *via* its nitrogen atom rather than oxygen in these new complexes as well as in the platinum(II) species $K_2[Pt(NH_2SO_3)_2X_2]$ (X = Cl, Br, or I). I.r. (and, where obtainable, Raman spectra) of the solids when compared with those of potassium sulphamate show that it is the $-NH_2$ modes (easily identified by their shifts on deuteriation) rather than the $-SO_3$ modes which are affected by co-ordination (see Table and Experimental section). The large shifts in the $-NH_2$ modes are similar to those found in mercury(II) amides,[9] while the much smaller shifts in $-SO_3$ modes are similar to those found in *S*-bonded thiosulphato-complexes.[10] A drop in the N–S stretching frequency from free to

---

[1] M. J. Cleare and W. P. Griffith, *Chem. Comm.*, 1968, 1302; *J. Chem. Soc.* (*A*), 1970, 1117.

[2] L. Brizard, *Compt. rend.*, 1896, **123**, 182.

[3] G. S. Reddy and P. Taimsalu, *Trans. Inst. Metal Finishing*, 1969, **47**, 187.

[4] L. Ramberg and S. Kallenberg, *Ber.*, 1912, **45**, 1512; H. Kirmreuther, *ibid.*, 1911, **44**, 3115.

[5] V. V. Lebedinskii, *Izv. Inst. Plat.*, 1947, **194**, 99.

[6] F. Ephraim and W. Flügel, *Helv. Chim. Acta*, 1924, **7**, 724.

[7] L. L. Po and R. B. Jordan, *Inorg. Chem.*, 1968, **7**, 526.

[8] J. N. Armor and H. Taube, *Inorg. Chem.*, 1971, **10**, 1570.

[9] N. Q. Dao and D. Breitinger, *Spectrochim. Acta*, 1971, **27A**, 905.

[10] G. W. Cox, T. M. Sabine, V. M. Padmanabhan, N. T. Ban, M. K. Chung, and A. K. Surjadi, *Acta Cryst.*, 1967, **23**, 578.

co-ordinated sulphamate is observed and would be expected for nitrogen co-ordination. In the imidosulphonate complex $Cs_4[Pt(NHSO_3)_2Cl_2]$ (made[4] by deprotonation of $[Pt(NH_2SO_3)_2Cl_2]^{2-}$), the N–S frequency rises to 886 cm^{-1} due presumably to the greater degree of N–S π-bonding attendant on the removal of a proton from the sulphamate amide group. The electronic spectrum of the rhodium complex $K_3[Rh(NH_2SO_3)Cl_5]$ is very similar to that of $K_2[Rh(NH_3)Cl_5]$, and indeed the latter complex may be made from the former by refluxing in aqueous solution, which again suggests *N*- rather than *O*-bonding of the $(NH_2SO_3)^-$ ligand. Attempts to prepare complexes of $CH_3SO_3^-$ from platinum metal halogeno-complexes and methanesulphonic acid or its salts were not successful, which again suggests that the isoelectronic $(NH_2SO_3)^-$ group probably co-ordinates *via* nitrogen; on chemical grounds one would expect the more basic nitrogen centre to co-ordinate preferentially.[7,8]

A curious feature of the reaction system sulphamic acid–platinum group halogeno-complexes is the formation, in very acid solutions, of plate-like crystals of $K_3[MCl_6],nNH_3SO_3$ (n = 0·9—1·1). The spectra of all four species (M = Rh, Ir, Ru, and Os) are very similar to each other and that of sulphamic acid in solution (*i.e.* the spectrum of sulphamic acid in the solid state is more complex than that of the solid 'complex'). *X*-Ray powder photographs for $K_3[RhCl_6],1{\cdot}1NH_3SO_3$ are quite different from those of $K_3[RhCl_6]$, solid sulphamic acid, potassium sulphamate, or potassium chloride; moreover the colour of $K_3[OsCl_6],NH_3SO_3$ (yellow) is quite different from that of $K_3[OsCl_6]$ (red). It seems probable that the zwitter-ion structure of sulphamic acid may be responsible, the lattice of the 'complex' containing distorted molecules of $[RhCl_6]^{3-}$ and $NH_3^+SO_3^-$ held together by dipole–dipole interaction or by N–H · · · Cl hydrogen bonds. A similar situation may exist in the double salt $K_2SO_4,2NH_3SO_3$ recently reported.[11] The failure to prepare analogous species with $K_3[MCl_6]$ and methanesulphonic acid also suggests that the zwitter-ion nature of sulphamic acid may be involved.

Prolonged refluxing of $K_3[Ru(NH_2SO_3)Cl_5]$ in aqueous solution gives $K_3[Ru_2NCl_8(H_2O)_2]$ and sulphite ion (simple pyrolysis of the ruthenium sulphamato-complex at 250° also gives the nitride). No such reaction is observed for the rhodium or iridium salts, but $K_3[Os(NH_2SO_3)Cl_5]$ gives a very low yield of a mixture of $K_3[Os_2NCl_8(H_2O)_2]$ and another nitrido-species, probably $K_5[Os_2NCl_{10}]$. The mechanism of the reaction with the ruthenium system is not clear; perhaps there is an oxidative two-electron process [*via* ruthenium(V)] of the type suggested by Chatt for formation of rhenium(V) nitrido-complexes with hydrazinium ion,[12] or possibly a disproportionation of ruthenium(III) to ruthenium(II) and (IV).[13]

EXPERIMENTAL

Potassium Sulphamatopentachlororhodate(III), $K_3[Rh(NH_2SO_3)Cl_5],H_2O$.—Hydrated sodium hexachlororhodate(III) (1·5 g) and potassium chloride (1·5 g) were dissolved in water (10 ml) and a saturated solution of sulphamic acid (1·2 g) added. The mixture was warmed for 2 min, cooled, and the light orange microcrystalline solid filtered off and washed with water and acetone (yield 80%) (Found: Cl, 34·3; K, 22·6; N, 3·4; S, 6·4. $H_4Cl_5K_3NO_4RhS$ requires Cl, 34·7; K, 22·9; N, 2·7; S, 6·3%). The complex is diamagnetic. Electronic spectrum (nm) reflectance: 475m, 395m; aqueous solution 475 (ε = 80), 382 (ε = 80). I.r. spectrum of normal salt: 3248m, 3143m, 1516m, 1293vs, 1252vs, 1151m, 1128m, 1058vs, 724s, 676w, 604w, 575m, 538m, 492m cm^{-1}.

Potassium Sulphamatopentachloroiridate(III), $K_3[Ir(NH_2SO_3)Cl_5],2H_2O$.—This was prepared in a similar manner to the rhodium salt but using hydrated sodium hexachloroiridate(III). The product is salmon-pink (yield 75%) (Found: Cl, 28·9; K, 19·0; N, 2·4; S, 4·8. $H_6Cl_5K_3IrNO_5S$ requires Cl, 28·7; K, 18·9; N, 2·3; S, 5·2%). The complex is diamagnetic. Electronic spectrum (nm) reflectance: 503m, 387m, 343m; solution 530w, 365vs, 330vs. I.r. spectrum of normal salt: 3234m, 3133m, 3013w, 1519m, 1290vs, 1259vs, 1169m, 1146m, 1058s, 723s, 700w, 612w, 575m, 538w, 498m, 309s, 295m, 255w cm^{-1}. Raman spectrum of normal salt: 326(10), 305(6), 258(2), 169(1) cm^{-1}; of deuteriate the same.

Potassium Sulphamatopentachlororuthenate(III) $K_3[Ru(NH_2SO_3)Cl_5]$.—Potassium hexachlororuthenate(III) (1 g) and sulphamic acid (1·2 g) were refluxed together in water (10 ml) for 15 min, and potassium chloride (1 g) then added to the mixture which was filtered while still hot. On cooling, the brown microcrystalline salt separated out; it was washed with water (5 ml) and then with acetone (yield 50%) (Found: Cl, 35·6; K, 23·3; N, 3·0; S, 6·6. $H_2Cl_5K_3NO_3SRu$ requires Cl, 36·1; K, 23·9; N, 2·9; S, 6·5%). Gram susceptibility (χ_g) 3·74 × 10^{-6} c.g.s.u. (25 °C) ($\mu_{eff.}$ 2·18 B.M.). I.r. spectrum: 3245m, 3143m, 3010w, 2289w, 1515m, 1290s, 1252s, 1150w, 1122m, 1057s, 726s, 658w, 595m, 573m, 537m, 486m, 323s, 306s, 284s, 272w cm^{-1}.

Potassium Sulphamatopentachloro-osmate(III), $K_3[Os(NH_2SO_3)Cl_5]$.—This was made by reaction of sodium hexachloro-osmate(IV) (0·9 g) and stannous chloride (0·49 g) in 25% hydrochloric acid (7 ml). This mixture was warmed with sulphamic acid (1 g) and potassium chloride (1·2 g); on cooling, yellow platelets of $K_3[OsCl_6],1{\cdot}1(NH_3SO_3)$ separated out. This (0·7 g) was warmed with sulphamic acid (1 g) and potassium chloride (1·2 g) in water (5 ml) under a nitrogen atmosphere. After 2 min yellow crystals of the product were formed and were filtered off (yield 40%) (Found: Cl, 31·1; K, 19·6; N, 2·4. $H_2Cl_5K_3NO_3SOs$ requires Cl, 30·5; K, 20·2; N, 2·4%). Gram susceptibility χ_g 3·27 × 10^{-6} c.g.s.u. ($\mu_{eff.}$ 2·21 B.M.). I.r. spectrum: 3230m, 3138m, 1517m, 1293vs, 1256vs, 1156m, 1139m, 1058vs, 721s, 674w, 598w, 511m cm^{-1}.

trans-*Potassium Bis*(*sulphamato*-N)-*dichloropalladate*(II), $K_2[Pd(NH_2SO_3)_2Cl_2]$.—Sulphamic acid (2 g) was added to a hot solution (10 ml) of potassium tetrachloropalladate(II) (2 g). The yellow precipitate was formed immediately (yield 80%) (Found: Cl, 15·6; N, 6·4. $H_4Cl_2K_2N_2O_6PdS_2$ requires Cl, 15·9; N, 6·0%). I.r. spectrum: 3180s, 3112s, 3040m, 1533m, 1265vs, 1240vs, 1168m, 1143m, 1054s, 758s, 734s, 626m, 585s, 541s, 508s cm^{-1}. Raman spectrum: 3182($\frac{1}{2}$), 3125(1), 1534($\frac{1}{2}$), 1272(1), 1248(2), 1165(1), 1066(3),

---

[11] S. Uchida and M. Mochizuki, *Chem. Letters* (*Japan*), 1972, **1**, 5.

[12] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (*A*), 1969. 2288.

[13] D. P. Rudd and H. Taube, *Inorg. Chem.*, 1971, **10**, 1543.

768(1), 708(1), 623(1), 578(½), 548(½), 496(2), 312(9), 269(1) cm^{-1}.

cis-*Potassium Bis(sulphamato-*N*)-dichloroplatinate*(II), $K_2[Pt(NH_2SO_3)_2Cl_2],2H_2O$.—This was made by the literature method [4] (Found: Cl, 12·5; N, 5·1; S, 10·6. $H_8Cl_2K_2N_2O_8S_2Pt$ requires Cl, 12·6; N, 5·0; S, 11·4%). I.r. spectrum: 3600s, 3498s, 3149s, 3115s, 3040m, 1614s, 1586s, 1551m, 1522m, 1295vs, 1266m, 1245m, 1180m, 1146m, 1123m, 1067vs, 1064s, 1055s, 1046s, 792m, 748s, 724s, 625m, 619m, 576s, 543m, 503m, 345w cm^{-1}. Raman spectrum: 3202(½), 3155(½), 1290(1), 1265(1), 1245(3), 1176(1), 1150(1), 1050(10), 1024(1), 1010(10), 792(1), 745(5), 622(3), 584(4), 545(1), 503(3), 376(1), 329(2), 325(10), 274(1) cm^{-1}.

trans-*Potassium Bis(sulphamato-*N*)-dichloroplatinate*(II), $K_2[Pt(NH_2SO_3)_2Cl_2]$.—This was made by the literature method [4] (Found: Cl, 13·2; N, 5·6. $H_4Cl_2K_2N_2O_6PtS_2$ requires Cl, 13·2; N, 5·2%). I.r. spectrum: 3168s, 3110s, 1534m, 1263vs, 1245vs, 1193m, 1153m, 1051s, 781w, 738s, 634w, 582s, 541m, 512s, 373m cm^{-1}. Raman spectrum: 3176(1), 3119(1), 1538(1), 1277(½), 1252(1), 1191(1), 1156(1), 1066(10), 764(4), 739(3), 648(1), 580(2), 544(½), 506(3), 366(1) cm^{-1}.

*Potassium Bis(sulphamato-*N*)-dibromoplatinate*(II), $K_2[Pt(NH_2SO_3)_2Br_2]$.—This was made by Kirmreuther's method [4] (Found: Br, 25·6; N, 4·6; S, 9·6. $H_4Br_2K_2N_2O_6PtS_2$ requires Br, 25·6; N, 4·5; S, 10·2%). I.r. spectrum: 3148s, 3129s, 3052m, 2420w, 1550m, 1524m, 1313vs, 1295vs, 1265vs, 1244s, 1194m, 1168w, 1065s, 727s, 626m, 578s, 545m, 520m, 505m, 382w, 287w cm^{-1}. Raman spectrum: 1280(1), 1250(1), 1070(10), 756(2), 743(10), 600(3), 577(2), 547(1), 500(5), 375(1), 283(3), 200(10) cm^{-1}.

*Potassium Bis(sulphamato-*N*)-di-iodoplatinate*(II), $K_2[Pt(NH_2SO_3)_2I_2]$.—This was made by the literature method [4] (Found: N, 4·1; S, 8·4. $H_4I_2K_2N_2O_6PtS_2$ requires N, 3·9; S, 8·9). I.r. spectrum: 3141m, 3120m, 3030m, 1538m, 1525m, 1310s, 1293s, 1260s, 1237s, 1188m, 1051s, 719s, 622w, 575s, 543m, 513m, 501m, 376w, 279m cm^{-1}.

Potassium Hexachlororhodate(III)-*Sulphamic Acid*, $K_3[RhCl_6],1\cdot1NH_3SO_3$.—Rhodium trichloride (hydrated; 1 g) was dissolved in hot concentrated hydrochloric acid and potassium chloride (1·5 g) and sulphamic acid (1·2 g) added. Shiny pink platelets of the salt were precipitated upon cooling the solution; they were washed in ethanol and acetone (yield 70%). Electronic spectrum, reflectance: 522m, 422m nm. I.r. spectrum: 3075s, 2955vs, 1547s, 1525s, 1389m, 1293s, 1279s, 1071vs, 999m, 692s, 542s, 518m, 343m cm^{-1}. Similar complexes of iridium, ruthenium, and osmium(III) may be prepared in like manner.

Caesium Bis(imidosulphamato)dichloroplatinate(II), $Cs_4[Pt(NHSO_3)_2Cl_2]$.—This was made by the literature method.[4] I.r. spectrum: 3244s, 1270m, 1140s, 1120s, 1008s, 886s, 770m, 720m, 635m, 580m, 510s, 311s, 280m cm^{-1}.

Potassium μ-Nitrido-octachlorodiaquodiruthenate(IV), $K_3[Ru_2NCl_8(H_2O)_2]$.—An aqueous solution of $K_3[Ru(NH_2SO_3)Cl_5]$ (0·5 g in 2 ml) was refluxed for two days; potassium chloride (2 g) was added to the solution and the brown crystals of the product filtered off (yield 80%).

Ammonium Amminopentachlororhodate(III), $(NH_4)_2[RhCl_5(NH_3)]$.—An aqueous solution of sulphamic acid (7 g) and of hydrated rhodium trichloride (3 g) were refluxed in water (30 ml) for two days. The solution was then evaporated to low bulk and conc. hydrochloric acid (5 ml) added. The brown crystals were filtered off and washed with water to remove $(NH_4)_3[RhCl_6]$ (Found: Cl, 51·4; N, 11·8. $H_{11}Cl_5N_3Rh$ requires Cl, 53·5; N, 12·6%). Electronic spectrum: reflectance 470m, 390m nm.

Electronic spectra were measured on a Cary 14 instrument (700—200 nm); i.r. spectra on a Perkin-Elmer 325 (4000—200 cm^{-1}) as Nujol mulls in caesium iodide plates. Raman spectra were measured (4000—160 cm^{-1} or, for weak scatterers, 400—160 cm^{-1}) on a Cary 81 instrument with a CRL 52MG laser (argon–krypton), using excitation at 6471 and at 5682 Å. Microanalyses were performed by the Microanalytical Department at Imperial College and by Alfred Bernhardt, Munich; potassium and ammonium were estimated as the tetraphenylborates.

We thank Miss J. Osborne for performing the *X*-ray powder diffraction work, and we thank Johnson, Matthey Ltd. for loan of platinum metal compounds. One of us (D. P.) acknowledges a C.A.P.S. award from the S.R.C. and Johnson, Matthey Ltd.

[2/2142 *Received, 13th September,* 1972]