Studies on Potassium Tri-μ-nitro-μ_3-oxo-*cyclo*-tris[nitroplatinate(II)] Trihydrate, Vèzes' Red Salt

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A new investigation of Vèzes' red salt, first prepared in 1893, indicates that it should be reformulated as $K_2[Pt_3(NO_2)_6O]\cdot 3H_2O$. Analytical, infrared, *X*-ray, and electrical-conductivity evidence suggests that the structure of the compound consists of planar anions arranged in a columnar stack resulting in the formation of linear chains of platinum atoms.

IN 1893 Vèzes reported that the reaction of dilute mineral acids with $K_2[Pt(NO_2)_4]$ resulted in the formation of copper-red needles which on the basis of elemental analysis and conductimetric titrations he formulated as $K_2H_4Pt_3(NO_2)_6O\cdot 3H_2O$.[1,2] The coppery nature of the product and the unusual empirical formula and oxidation state of the platinum atoms as formulated by Vèzes suggested that this compound might possess similar properties to the Krogmann class of compounds such as $K_2Pt(CN)_4Br_{0.3}\cdot 3.2H_2O$.[3] The latter compound has received much study recently since it possesses one-dimensional metallic properties at room temperature.[4] In view of the current interest in this type of compound we have therefore re-examined Vèzes' red salt, compound (1), both in solution and in the solid state and the results of this investigation suggest that it possesses a most unusual solid-state structure.

RESULTS AND DISCUSSION

Compound (1) is obtained by heating $K_2[Pt(NO_2)_4]$ with hot dilute sulphuric acid. During the reaction the colour of the solution changes slowly from pale blue to deep green and is accompanied by the evolution of oxides of nitrogen. The reaction occurs slowly and the mixture has to be heated for 30 min otherwise unchanged $K_2[Pt(NO_2)_4]$ as well as the red product will crystallise from the cooled reaction mixture. Humphreys and Staples [5] showed that the first stage of this reaction is a fast protonation of a nitro-group followed by breakdown of the protonated compound to form $[Pt(NO_2)_3(OH_2)]^-$ ions. The nature of the further reactions prior to the formation of the red product is not known.

Analytical results for the red product are shown in Table 1 together with those reported by Vèzes.[1] The compound has a Pt : N ratio of 1 : 2 and it is of prime importance to determine the oxidation state of the platinum. The common chemical methods involving oxidative titrations cannot be applied because nitrite ions are liberated by ligand-substitution reactions. The *X*-ray photoelectron (*X*-p.e.) spectrum of the platinum 4*f* electrons in (1) contains only two peaks which occur in the same positions as those observed in the spectrum of $K_2[Pt(NO_2)_4]$. This indicates that the platinum in (1) is present only in the oxidation state II.

Vèzes postulated the existence of four protons in the solid-state structure on the basis of conductimetric titrations. However, it is hard to reconcile the presence of four protons in the structure with a platinum(II) compound. The red solid does not give an immediate colour change with damp blue litmus paper and in addition the acidic nature of solutions of (1) can be accounted for by its hydrolysis in water as will be discussed later. We therefore conclude that the red salt should be formulated as the platinum(II) compound $K_2[Pt_3(NO_2)_6O]\cdot 3H_2O$.

The very unusual empirical formula implies that the platinum atoms can exist in the preferred square-coplanar co-ordination only if the compound contains bridging nitro-ligands. We attempted to deduce the solid-state structure by examining the breakdown products in water and by studying relevant solid-state properties. Unfortunately no single crystals suitable for detailed *X*-ray examination could be obtained.

TABLE 1

Analytical results (%) for compound (1)

Compound	Pt	K	H	H_2O	N
Found by Vèzes after drying at 105 °C	60.9	8.1	0.50		8.85
Calc. for $K_2[Pt_3(NO_2)_6O]$	61.35	8.20	0.0		8.80
Found in present work after drying at 25 °C		7.75 [a]	1.0 [b]	5.0 [c]	8.30 [b]
Calc. for $K_2[Pt_3(NO_2)_6O]\cdot 3H_2O$		7.75	0.60	5.3	8.35

[a] By flame photometry. [b] By microanalysis. [c] By thermal gravimetric analysis.

Compound (1) is only slightly soluble in cold water but is readily soluble in hot water to give a yellow solution. In aqueous solution it reacted with ammonia in a mole ratio of 1 : 6 to yield *cis*-$[Pt(NO_2)_2(NH_3)_2]$, and similarly with 4 mol of potassium hydroxide followed by oxalic acid to yield *cis*-$[Pt(NO_2)_2(O_4C_2)]^{2-}$. The high yield (80%) of product in the latter reaction and the production of *cis*-dinitro-complexes in both cases suggest that all the platinum atoms in solution are co-ordinated by two *cis*-nitro-ligands. From the empirical formula of (1) and the results described above it seems likely that in the solid state the compound contains platinum atoms co-ordinated by two *cis*-nitro-ligands, one of which forms a bridge to another *cis*-dinitroplatinum(II) group.

The i.r. absorption frequencies of (1) observed between

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[1] M. Vèzes, *Ann. Chim. Phys.*, 1893, **6**, 29, 160.

[2] M. Vèzes, *Z. anorg. Chem.*, 1897, **14**, 278.

[3] K. Krogmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 35; C. Peters and C. F. Eagen, *Inorg. Chem.*, 1976, **15**, 782.

[4] H. R. Zeller, *Adv. Solid-state Phys.*, 1973, **13**, 31.

[5] D. Humphreys and P. J. Staples, *J. Chem. Soc.* (*A*), 1970, 2708.

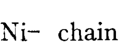
450 and 4 000 cm^{-1} together with their assignments are shown in Table 2. The absorption bands at 1 425, 1 337, 840, 598, and 587 cm^{-1} correspond to those observed in the *spectrum* of $K_2[Pt(NO_2)_4]$ and indicate the presence of terminal N-donor nitro-ligands in (1).[6] The additional absorption bands observed for (1), however, cannot be assigned to any common terminal ligands or ions allowed by the empirical formula of the complex, *e.g.* NO, ONO, NO_3, *etc.*, but, again, suggest instead the presence of bridging ligands. The absorptions at 1 537 and 1 148 cm^{-1} may be due to the asymmetric and symmetric N–O stretching frequencies respectively of bridging nitro-ligands.[6,7] The observation that these absorptions are split to a greater extent in (1) than in $[(H_3N)_3Co(\mu\text{-}NO_2)(\mu\text{-}OH)_2Co(NH_3)_3]^{3+}$ may be due to the stronger metal–ligand bonding expected in the platinum complex.[6] The spectrum of (1) may also be compared with that of $[NMe_4][Ni(NO_2)_3]$ in which  $-Ni-N-\overset{\overset{\displaystyle O}{\|}}{O}-Ni-$ chains are proposed and for which absorption bands are observed at 1 435 and 1 202 cm^{-1}.[8] The greater splitting observed for (1) may be due to the presence of strong coupling between the bridging NO_2 groups. The origin of the strong band at 1 086 cm^{-1} is unknown but this band is also present in the spectrum of the hydrolysis product $K_2[Pt(NO_2)_2(OH)_2]$ and cannot therefore be due to a structural feature of (1).

TABLE 2

Infrared absorption bands (400—4 000 cm^{-1})

Vèzes' red salt	$K_2[Pt(NO_2)_4]$ [6]	$K_2[Pt(NO_2)_2(OH)_2]$	Assignment
3 615,		3 570, 3 300	Lattice water
3 628s,		1 605m	
3 545,			
3 436m			
1 537s			ν_{asym}(N–O) Bridging NO_2
1 425s	1 436, 1 410	1 452s	ν_{asym}(N–O) Terminal NO_2
1 337s	1 350	1 340, 1 300m	ν_{sym}(N–O) Terminal NO_2
1 148m			ν_{sym}(N–O) Bridging NO_2
1 086s		1 090s	
881m			
840m	838, 832	841m, 835m	δ Terminal NO_2
702m			
598,	636, 613	640m, 627m	ρ Terminal NO_2
587m		558m	
	450m	485m	

The *X*-ray diffraction lines of a powdered sample of (1) are shown in Table 3. Analysis of the lines indicates a relatively small hexagonal unit cell of dimensions $a = b = 10.25$, and $c = 3.32$ Å. The determination of the density of (1) was difficult due to the very powdery nature of the product but a value of *ca.* 5 g cm^{-3} was obtained using a pyknometer. This compares with a calculated value of 5.46 g cm^{-3} assuming three platinum atoms per unit cell. An unambiguous determination of the structure of (1) must ultimately depend on a more detailed *X*-ray study but from the evidence presented so far and from a study of molecular models two structures appeared possible. In both cases the anion contains a central oxide ion co-ordinated to the three platinum atoms, each platinum atom achieving the preferred square-coplanar environment with bridging and terminal nitro-groups.

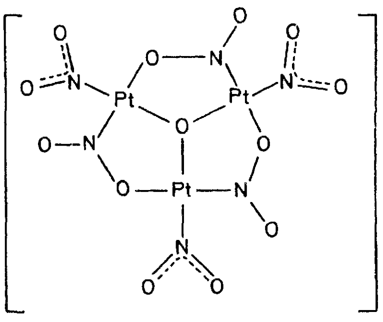
TABLE 3

X-Ray powder data for $K_2[Pt_3(NO_2)_6O]\cdot 3H_2O$

		$10^4 \sin^2 \theta$		
Line no.	Intensity	obs.	calc.*	Assignment
1	vvs	57	56.5	100, 010
2	m	170	170	110
3	s	227	226	200, 020
4	vvs	394	395	210, 120
5	vs	506	508	300, 030
6	s	539	540	001
7	vvs	597	597	011, 101
8	w	677	678	220
9	vvs	735	735	310, 130
10	w	767	766	021, 201
11	s	897	904	400, 040
12	w	934	935	121, 211
13	m	1 046	1 048	301, 031
14	m	1 066	1 073	320, 230
15	m	1 184	1 186	410, 140
16	w	1 213	1 218	221
17	m	1 270	1 275	131, 311
18	vw	1 411	1 413	500, 050
19	m	1 444	1 444	401, 041
20	w	1 514		Unassigned
21	w	1 571	1 582	420, 240
22	vw	1 607	1 614	321, 231

* Based on a hexagonal unit cell with dimensions $a = b = 10.25$, and $c = 3.317$ Å.

In one model the ion has an overall trigonal-pyramid shape with the oxide ion at the apex and in the other, (A), the ion is essentially planar with an sp^2-hybridised oxide ion in the centre. Structure (A) is preferred since the observed small ' *c* ' dimension of the unit cell is only compatible with the $[Pt_3(NO_2)_6O]^{2-}$ ion being approximately planar and this also favours columnar stacking of the anion (see later). Although three-co-ordinate oxide as postulated here does not occur commonly it is found in the ions $[M_3O(O_2CMe)_6L_3]^+$ (M = Mn, Cr, Ru, or Fe) [9]



(A)

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[6] K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, 1958, **80**, 4817.

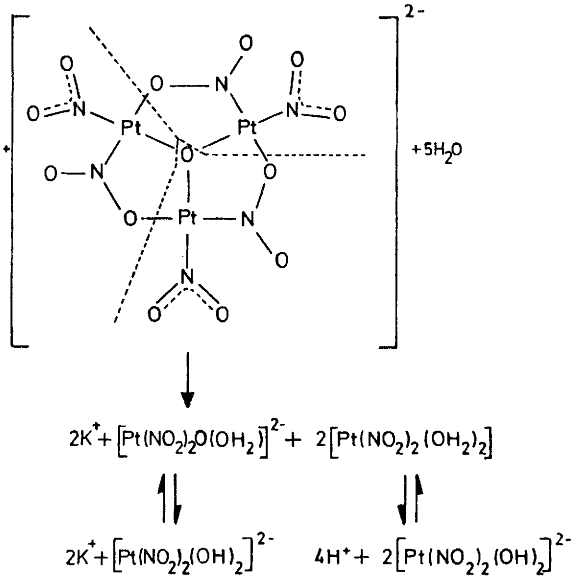
[7] J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 1959, 4073.

[8] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1967, **6**, 813.

[9] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, London, 1972, p. 408.

and $[(HgMe)_3O]^+$,[10] and has been postulated in the ion $[Ir_3O(SO_4)_9]^{10-}$.[11] Studies of molecular models indicate that the nitro-groups do not have to be coplanar with the plane of the three platinum atoms.

Acid-base and conductimetric titrations reported by Vèzes show that aqueous solutions of (1) contain four acidic protons per mol of the solid.[1] The acidity of aqueous solutions of the compound can be explained from our structural model for the anion. We propose that dissolution of the anion is accompanied by cleavage of the bridging ligands and depolymerisation as shown in the Scheme. The acidity of the solutions can then be related to the hydrolysis of the neutral species *cis*-$[Pt(NO_2)_2(OH_2)_2]$ which results in the formation of four protons per anion as found by Vèzes.[1] In support of this reaction scheme, the product of the complete neutralisation of (1) by K[OH] appears on analytical and i.r. evidence to be $K_2[Pt(NO_2)_2(OH)_2]$ (see Experimental section) as expected from the Scheme.



SCHEME

The *X*-ray data suggest that the planar cyclic anions proposed for (1) form a columnar stacked structure similar to those found in many square-planar d^8 metal complexes.[12] In the case of (1) the stacking along the *c* axis would lead to a compound containing three linear chains of platinum atoms per stack with intrachain metal–metal distances of 3.32 Å. The short metal–metal distances in many columnar stacked platinum(II) compounds result in unusual colours for these compounds and in semiconducting properties along the axis of the stack.[12] The red colour of solid (1) in contrast to its yellow aqueous solutions therefore suggests this structure. We briefly examined the electrical properties of (1) and found that compressed pellets behave as semiconductors with room-temperature d.c. conductivities of 10^{-6} S cm^{-1}. The d.c. conductivity of the compound at room temperature is approximately two orders of magnitude less than that observed in the platinum(II) chain complex $[Pt(NH_3)_4][PtCl_4]$ which has a metal–metal distance of 3.25 Å.[13] The lower conductivity observed for (1) is probably related to its greater metal–metal distance (3.32 Å). Thus the electrical conduction properties of the compound are in agreement with the suggestion that it is a platinum(II) chain compound.

Conclusions.—The evidence presented suggests that the compound $K_2[Pt_3(NO_2)_6O]\cdot3H_2O$, first prepared by Vèzes, has a solid-state structure containing columnar stacked cyclic anions which results in platinum(II) chain formation and is quite different from the Krogmann class of compound. The compound is only one member of a series of complex nitroplatinates whose unusual colours and stoicheiometries vary with the cation present.[14] All are obtained from acidic solutions of tetranitroplatinates(II) suggesting that they are formed by similar mechanisms and have closely related structures and properties.

EXPERIMENTAL

Potassium Tetranitroplatinate(II), $K_2[Pt(NO_2)_4]$.—This compound was prepared from $K_2[PtCl_4]$ and was twice recrystallised from hot water[15] {Found: N, 11.9. Calc. for $K_2[Pt(NO_2)_4]$: N, 12.2%}.

Potassium Tri-μ-nitro-μ₃-oxo-cyclo-*tris[nitroplatinate*(II)] *Trihydrate*, $K_2[Pt_3(NO_2)_6O]\cdot3H_2O$ (1).—This compound was prepared by the method of Vèzes.[1,2] The compound $K_2[Pt(NO_2)_4]$ (13.0 g) was treated with 1 mol dm^{-3} sulphuric acid (13.1 cm^3) and the resulting blue solution was diluted to 30 cm^3 and warmed until all the solid had dissolved. The solution was concentrated to *ca*. 5 cm^3 with the evolution of oxides of nitrogen. Cooling of the resulting green solution to room temperature yielded the red product which was twice recrystallised from hot water to remove any potassium sulphate impurity. The product was obtained as microscopically small thin orange-red needles and was dried in air at room temperature (for analytical results see Table 1).

Reactions of (1).—*With* NH_3. Compound (1) (0.50 g, 4.95×10^{-4} mol) was dissolved in warm water (5 cm^3) and treated with 1 mol dm^{-3} aqueous ammonia (3.2 cm^3, 3×10^{-3} mol). Almost immediately, a dense white crystalline precipitate began to form. After cooling to 5° C the solution was filtered and the product washed with a little ice-cold water and dried in air at room temperature, yield 0.22 g (44%) {Found: H, 1.95; N, 17.5. Calc. for $[Pt(NO_2)_2(NH_3)_2]$: H, 1.90; N, 17.45%}. The i.r. spectrum of the product in the 450—4 000 cm^{-1} region was identical to that reported for *cis*-$[Pt(NO_2)_2(NH_3)_2]$.[16]

With $K_2[C_2O_4]$. Compound (1) (0.40 g, 3.96×10^{-4} mol) and KOH (0.10 g, 1.8×10^{-3} mol) were dissolved in warm water (7.5 cm^3). Oxalic acid (0.160 g, 1.8×10^{-3} mol) was added and the warm solution evaporated to half its volume.

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[11] C. K. Jørgenson, *Acta Chem. Scand.*, 1959, **13**, 196.

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[14] L. F. Nilson, *Ber.*, 1877, 1722.

[15] I. V. Matsko, G. A. Shagisultanova, and Yu. E. Selyaninov, *Russ. J. Inorg. Chem.*, 1965, **10**, 689.

[16] A. V. Babaeva, O. N. Evstaf'eva, and Yu. Ya. Kharitonov, *Russ. J. Inorg. Chem.*, 1962, **7**, 15.

On cooling, the concentrated solution yielded a yellow crystalline product which was filtered off and washed with a little ice-cold water. The product was dried in air at room temperature, yield 0.492 g (80%) {Found: C, 5.10; H, 0.55; N, 5.70. Calc. for $K_2[Pt(NO_2)_2(O_4C_2)]$: C, 4.90; H, 0.80; N, 5.70%}. The i.r. spectrum of the product was identical to that of an authentic sample of $K_2[Pt(NO_2)_2(O_4C_2)]$ prepared by the method of Vèzes.[17]

With KOH. Compound (1) (0.40 g, 3.96×10^{-4} mol) was dissolved in warm water (5 cm^3) and KOH (93.5 mg, 1.6×10^{-4} mol) added. Acetone (*ca.* 50 cm^3) was added and the solution was set aside for 2 days. The creamy yellow crystalline precipitate was filtered off, washed with diethyl ether, and dried in air at room temperature {Found: H, 0.3; N, 7.0. Calc. for $K_2[Pt(NO_2)_2(OH)_2]$: H, 0.5; N, 7.00%}.

Physical Measurements.—*X*-Ray powder photographs were taken with a Debye–Scherer camera using Cu-K_α radiation. Infrared spectra were recorded as Nujol or halogenocarbon oil mulls using a Perkin–Elmer 225 spectrometer. Electrical-conductivity studies were made as previously described.[13]

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[17] M. Vèzes, *Compt. rend.*, 1897, **125**, 525.