Co-ordination Chemistry of Higher Oxidation States. Part 26.[1] Spectroscopic Studies of Tellurate Complexes of the Trivalent Group 1B Metals. *X*-Ray Structure of $Na_5[Cu\{TeO_4(OH)_2\}_2]\cdot16H_2O$ †

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The structure of $Na_5[Cu\{TeO_4(OH)_2\}_2]\cdot16H_2O$ has been determined by *X*-ray structure analysis. It crystallises in the triclinic space group $P\bar{1}$ with a = 5.922(4), b = 8.939(2), c = 12.528(2) Å, α = 98.45(1), β = 99.11(3), γ = 93.82(4)°, and Z = 1. The structure was refined to R = 0.040 for 2 131 observed reflections [$F > 3\sigma(F)$]. The composition of the crystal examined was deficient in sodium leading to a proposed formula $Na_{5-x}H_x[Cu\{TeO_4(OH)_2\}_2]\cdot16H_2O$ (x = 0.64). The discrete centrosymmetric anion contains Cu^{III} with approximately square-planar CuO_4 groups linked by *trans* edges to $TeO_4(OH)_2$ octahedra [Cu–O 1.833(4) and 1.839(4) Å]. The $[M\{TeO_4(OH)_2\}_2]^{5-}$ ions (M = Cu, Ag, or Au) have been studied by i.r., u.v.–visible, and n.m.r. (^{125}Te, ^{109}Ag, and ^{17}O) spectroscopy. For $[Ag\{TeO_4(OH)_2\}_2]^{5-}$ the ^{125}Te n.m.r. signal (+774 p.p.m.) is a doublet [$^2J(^{107,109}Ag-^{125}Te)$ = 73 Hz]. For the silver(III) ions $[Ag\{TeO_4(OH)_2\}_2]^{5-}$ and $[Ag\{IO_5(OH)\}_2]^{5-}$ the ^{109}Ag n.m.r. signals occur at *ca.* +2 800 p.p.m. from Ag^+ (aq).

Copper(III) and silver(III) compounds with periodate or tellurate were reported in the early years of this century,[2,3] but their formulation as co-ordination complexes is due to Malatesta[4] who suggested octahedrally co-ordinated metal ions bound to tridentate (*fac*) $EO_6{}^{n-}$ ions (E = I or Te). General formulations $M_xH_yM'(IO_6)_2\cdot nH_2O$ (M = Na or K, M′ = Cu or Ag, $x + y = 7$) and $M_{x'}H_{y'}M'(TeO_6)_2\cdot nH_2O$ ($x' + y' = 9$) were established.[4–6] More recent workers[7,8] have suggested that protonated $HIO_6{}^{4-}$ or $H_2TeO_6{}^{4-}$ are the ligand forms present, and the *X*-ray structure[9] of $K_5[Ag(HIO_6)_2]\cdot8H_2O$ revealed planar four-co-ordinate silver. In spite of continuing uncertainties about their formulation and structures, these complexes have found some use in analytical chemistry as oxidants.[2,10] Here we report the *X*-ray structure of a sodium copper tellurate complex and spectroscopic data on it and related complexes.

Experimental

Multinuclear n.m.r. spectra were recorded on a Bruker AM360 instrument. The solutions were contained in a tube (outside diameter 10 mm) fitted with a co-axial tube (outside diameter 5 mm) containing D_2O to provide the lock. Spectra were obtained from aqueous alkali solutions (*ca.* 2 mol dm^{-3} NaOH) at 25 °C. Tellurium-125 (113.6 MHz), ^{63}Cu (95.4 MHz), ^{109}Ag (16.75 MHz), and ^{17}O (48.8 MHz) were referenced to external neat $TeMe_2$ (δ = 0), $[Cu(MeCN)_4]^+$ in MeCN (δ = 0), 9.1 mol dm^{-3} Ag^+ (aq) in water (δ = −47),[11] and water (δ = 0) respectively, and are reported using the high-frequency-positive convention.

Analyses.—Atomic ratios of Na, Cu, Ag, Te, and Au were determined by energy-dispersive *X*-ray spectroscopy (e.d.x.s.) using a standard (EDAX) system connected to a Cambridge Stereoscan 150. Sodium and Cu were also determined spectrophotometrically, and the water contents were estimated by thermogravimetric analysis (t.g.a.) on a Stanton Redcroft TG/750/770 thermobalance. The sodium copper tellurate samples were prepared by the literature route,[8] and were obtained as brown crystals by precipitation with aqueous $NaNO_3$ solution. Typical analyses: Found for sample 1: Cu, 7.0; Na, 11.4; H_2O, 37.5%; atom ratio Na:Cu:H_2O 4.52:1.0:19; e.d.x.s. atomic ratio Na:Cu:Te 4.54:1.0:1.98. Found for sample 2: e.d.x.s. atomic ratio Na:Cu:Te 5.3:1.0:2.2. H_2O, 12.2. $Na_5[Cu\{TeO_4(OH)_2\}_2]\cdot16H_2O$ requires Cu, 6.9; Na, 12.5; Te, 13.9; H_2O, 31.4%.

The silver and gold analogues and sodium silver periodate were also made by literature routes.[8,12]

Crystal Structure Determination.—Brown-yellow lath-like crystals were obtained from the reaction mixture. The crystals are dichroic and of poor quality but recrystallisation proved impossible. Preliminary photographic *X*-ray examination established the crystal system and cell volume.

Crystal data. $H_{36+x}CuNa_{5-x}O_{28}Te_2$ (x = 0.64), M = 917.98,‡ triclinic, a = 5.922(4), b = 8.939(2), c = 12.528(2) Å, α = 98.45(1), β = 99.11(3), γ = 93.82(4)°, U = 645.0 Å^3, D_m = 2.35(2) (flotation in CCl_4–$CHBr_3$), Z = 1, D_c = 2.363‡ g cm^{-3}, $F(000)$ = 448,‡ space group $P\bar{1}$, $\lambda(Mo\text{-}K_\alpha)$ = 0.710 69 Å, $\mu(Mo\text{-}K_\alpha)$ = 32.3 cm^{-1}.‡

Accurate cell dimensions were obtained from 25 accurately centred reflections on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo-K_α radiation. A room-temperature crystal (0.75 × 0.25 × 0.1 mm) mounted in a thin-wall glass capillary was used to obtain 2 249 reflections [$1.5 < \theta < 25°$, h(0—7), k(−10 to +10), l(−14 to +14)]. A very small amount of decay was observed in the check reflections and a psi-scan empirical absorption correction was applied to the data (transmission: maximum 99.98; minimum 75.60%). There were no systematic absences and after data reduction there were 2 249 unique reflections of which 118 with $F < 3\sigma(F)$ were omitted leaving 2 131 used in the solution and refinement.

Structure determination. The copper and tellurium atoms were easily located from the Patterson synthesis and although the analysis was started in space group $P1$ it soon became clear that $P\bar{1}$ was the correct choice. The anion oxygen atoms were readily located from structure-factor and electron-density syntheses and subsequent calculations located the sodium and

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† Pentasodium 1,1,3,3-tetrahydroxo-1,2;1,2;2,3;2,3-tetra-μ-oxo-1,1,3,3-tetraoxo-1,3-ditellurium-2-cuprate(III) hydrate (1/16).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ Based on x = 0.

oxygen atoms of the water molecules. It was apparent that Na(3) was anomalous; its height in the Fourier difference maps was substantially lower than those of Na(1) and Na(2) and least-squares refinement gave a large isotropic thermal parameter (0.11 Å^2). Several possibilities exist including: Na(3) is actually an oxygen atom; Na(3) is partially occupied, charge balance being maintained by an additional H^+. Replacing Na(3) by an oxygen atom still gave a rather large thermal parameter compared to the other oxygen atoms and evidence supporting Na(3) as a sodium ion came from an examination of the geometry of the surrounding oxygen atoms [Na(3) $\cdots$ O *ca.* 2.4 Å]. The most plausible chemical model thus emerged with Na(3) as a partially occupied site. With a fixed isotropic thermal parameter [typical of Na(1) and Na(2)] and a refined population parameter for Na(3), least-squares refinement converged to R = 0.040 (R' = 0.061) {121 parameters, 2 131 reflections, anisotropic atoms, except Na(3) and water O, $w = 1/[\sigma^2(F) + 0.0001 F^2]$, max shift/error 0.1}. Residual electron-density features in the range 2.3 to −1.3 e Å^{-3}. No hydrogen atoms were included in the model.

Scattering factors for neutral atoms and anomalous dispersion terms were taken from ref. 13 (Te, Cu, and Na) and SHELX[14] (O). Final atomic co-ordinates and selected bond lengths and angles are presented in Tables 1 and 2. All calculations were carried out on the Southampton University IBM 3090-150 computer using the programs SHELX,[14] PLUTO,[15] ORTEP,[16] and XANADU.[17]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Several samples of the sodium copper(III) tellurate complex were made by peroxodisulphate oxidation of a mixture of Cu^{2+} and H_6TeO_6 in aqueous alkali, followed by addition of concentrated sodium nitrate solution.[8] The chocolate-brown crystalline products were analysed by a combination of e.d.x.s. and conventional wet methods with t.g.a. used to estimate* the water content. The Cu:Te ratio was constant at 1:2, but the sodium content appeared to vary with the sample, Na:Cu = 4—5:1, with the water content highly variable, H_2O:Cu = 12—20:1. These results are generally consistent with other studies[4,6,8] and lead to an ideal composition $Na_5[Cu\{TeO_4(OH)_2\}_2]\cdot nH_2O$ with the samples deficient in Na presumed to have H_3O^+ to balance the charges. In this work we did not observe materials with a high sodium content which occasionally have been reported *e.g.* $Na_9Cu(TeO_6)_2\cdot 20H_2O$.[5]

The pure solid complex is stable for some months, although impure samples deteriorate in days. The complex is moderately soluble in water or dilute alkalis (*ca.* 2 mol dm^{-3}), insoluble in concentrated alkali, and immediately decomposed to Cu^{II} by mineral acids and organic solvents. Solutions in dilute NaOH decompose slowly at room temperature (*ca.* 10% in 24 h as estimated by ^{125}Te n.m.r. spectroscopy, see below).

The Structure of $Na_5[Cu\{TeO_4(OH)_2\}_2]\cdot 16H_2O$.—Several copper tellurate structures have been described involving Cu^{II} and Te^{VI}.[18,19] In these compounds the tellurium is octahedrally co-ordinated by oxygen and as expected the copper atom has a square-planar or distorted-octahedral co-ordination. The present compound contains the rare Cu^{III} in a discrete anion $[Cu\{TeO_4(OH)_2\}_2]^{5-}$ in which a square-planar CuO_4 group

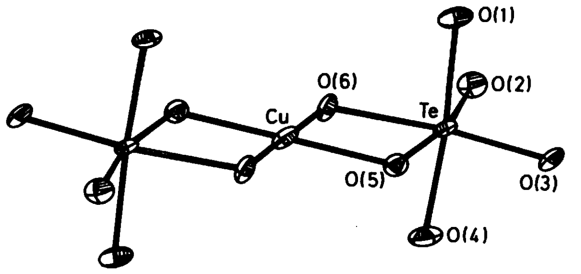

Figure 1. The anion showing the atom-numbering scheme and with atoms drawn with a 50% probability surface

Table 1. Atomic co-ordinates for $Na_5[Cu\{TeO_4(OH)_2\}_2]\cdot 16H_2O$

Atom	x	y	z
Te	0.170 94(6)	0.231 54(4)	0.186 07(3)
Cu	0.000 0	0.000 0	0.000 0
Na(1)	0.329 9(5)	0.227 7(3)	0.680 0(2)
Na(2)	0.338 1(5)	0.328 5(3)	−0.049 6(2)
Na(3)*	0.000 0	0.000 0	0.500 0
O(1)	−0.127 8(7)	0.184 8(5)	0.234 2(4)
O(2)	0.134 2(8)	0.437 0(5)	0.206 4(4)
O(3)	0.336 2(7)	0.217 7(5)	0.322 6(4)
O(4)	0.453 1(7)	0.271 9(5)	0.126 5(4)
O(5)	0.164 0(8)	0.013 5(5)	0.138 5(4)
O(6)	0.010 1(8)	0.207 6(5)	0.035 7(4)
O(7)	0.725 7(9)	0.422 4(6)	−0.046 1(4)
O(8)	0.406 3(9)	0.102 1(6)	0.843 7(4)
O(9)	0.265 1(8)	0.445 7(5)	−0.211 2(4)
O(10)	−0.057 7(9)	0.120 4(6)	0.677 4(4)
O(11)	0.716 1(9)	0.389 4(5)	0.419 8(4)
O(12)	0.658 6(9)	0.347 1(6)	0.637 1(4)
O(13)	0.134 7(10)	0.263 3(6)	0.499 1(4)
O(14)	0.387 8(12)	−0.023 1(7)	0.590 4(6)

* Thermal parameter fixed and population refined to 0.361(5).

Table 2. Selected distances (Å) and angles (°)

Te–O(1)	1.996(4)	Cu–O(5)	1.833(4)
Te–O(2)	1.849(4)	Cu–O(6)	1.839(4)
Te–O(3)	1.856(4)	Te $\cdots$ Cu	2.881(1)
Te–O(4)	1.968(4)	Na(3) $\cdots$ O(10)	2.408(5)
Te–O(5)	1.948(4)	Na(3) $\cdots$ O(13)	2.436(5)
Te–O(6)	1.946(4)	Na(3) $\cdots$ O(14)	2.431(7)
Na(1) $\cdots$ O(8)	2.475(6)	Na(2) $\cdots$ O(4)	2.342(5)
Na(1) $\cdots$ O(9‴)	2.300(6)	Na(2) $\cdots$ O(6)	2.608(5)
Na(1) $\cdots$ O(10)	2.422(6)	Na(2) $\cdots$ O(7)	2.382(6)
Na(1) $\cdots$ O(12)	2.332(6)	Na(2) $\cdots$ O(7″)	2.451(6)
Na(1) $\cdots$ O(13)	2.451(6)	Na(2) $\cdots$ O(8⁗)	2.352(6)
Na(1) $\cdots$ O(14)	2.426(7)	Na(2) $\cdots$ O(9)	2.407(6)
O(1)–Te–O(2)	91.1(2)	O(3)–Te–O(4)	92.1(2)
O(1)–Te–O(3)	92.1(2)	O(3)–Te–O(5)	91.7(2)
O(1)–Te–O(4)	175.4(2)	O(3)–Te–O(6)	169.5(2)
O(1)–Te–O(5)	86.0(2)	O(4)–Te–O(5)	92.1(2)
O(1)–Te–O(6)	89.2(2)	O(4)–Te–O(6)	86.3(2)
O(2)–Te–O(3)	99.5(2)	O(5)–Te–O(6)	77.9(2)
O(2)–Te–O(4)	89.9(2)	Cu–O(5)–Te	99.2(2)
O(2)–Te–O(5)	168.6(2)	Cu–O(6)–Te	99.1(2)
O(2)–Te–O(6)	91.0(2)	O(5)–Cu–O(6)	83.7(2)
		O(5)–Cu–O(6′)	96.3(2)

Symmetry: (′) $-x, -y, -z$; (″) $1 - x, 1 - y, -z$; (‴) $x, y, z + 1$; (⁗) $x, y, z - 1$.

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* Only approximate water contents are given by t.g.a. since the final weight loss is ill defined and it is likely that some oxygen loss accompanies the dehydration.

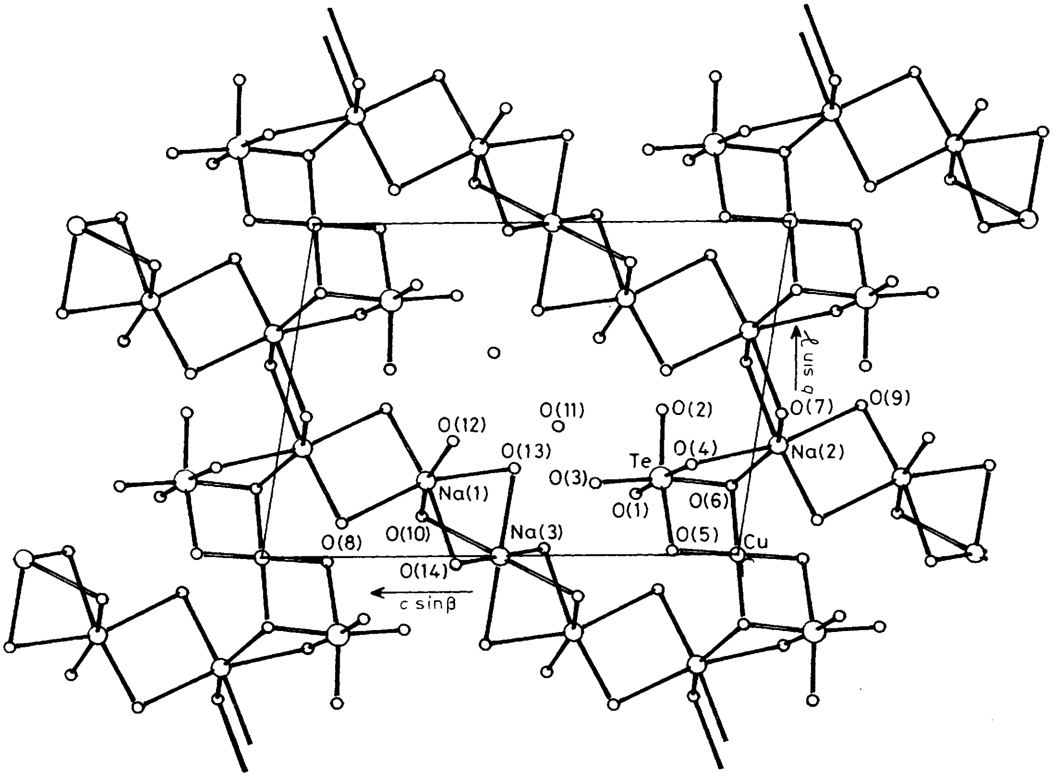

Figure 2. Unit-cell diagram viewed from the *a* direction showing the atom-numbering scheme and atoms drawn with arbitrary size

is linked by *trans* edge sharing to two 'TeO_6' octahedra (see Figure 1). The ion is centrosymmetric and although the hydrogen atoms were not located in the *X*-ray analysis, i.r. spectroscopy indicates their presence in the anion. Comparison of the six Te–O distances (Table 2) with published structures of the dimeric edge-linked anions, *e.g.* $[Te_2O_6(OH)_4]^{4-}$,[20] leads to the conclusion that the two shortest distances to O(2) and O(3) are terminal Te–O bonds and the two longest to O(1) and O(4) are Te–O(H). The two remaining distances, only a little shorter than the longest, are involved in the bridging bonds to Cu. The square-planar stereochemistry at the Cu^{III} is very similar to that found for $KCuO_2$[21] in which *trans* edge-linked chains were reported. The Cu–O distance (1.84 Å) is very similar to that found in the present compound and shorter by *ca.* 0.1 Å than Cu–O distances in the copper(II) tellurates. The within-ring angles of the four-membered $\overline{\text{MOM'O}}$ ring (M, M′ = Cu or Te) in the present compound are similar to those in $KCuO_2$ (OCuO 84.5°) and several edge-linked TeO_6 octahedra [*e.g.* OTeO 76.9(7)° in Na_2TeO_4[22]]. The shortest non-bonded O ··· O distance in the anion [O(5) ··· O(6) 2.45 Å] is also found in the ring. These four atoms are not quite coplanar with a dihedral angle of 3.2° between the CuO(5)O(6) and TeO(5)O(6) planes thus creating a slightly 'stepped' structure for the anion. This arrangement is very similar to that in the anion $[Ag\{IO_5(OH)\}_2]^{5-}$ (ref. 9) and provides another example of the structural similarity between Te and I in their oxo species. In the silver compound the shortest anion-to-anion distance (2.70 Å) was used to support a hydrogen-bonding scheme. This may be compared with the O ··· O distances in $Te(OH)_6$[23] (2.64 and 2.77 Å) and the shortest interanion distance of 2.84 Å in the present compound [O(1) ··· O(4), O(4) at $x - 1, y, z$].

Figure 2 shows the packing diagram and in particular the sodium ions and water molecules. Of the three sodium cations in the asymmetric unit, two appear normal while the third on the special position 0,0,½ has a large thermal parameter. This was interpreted as a fractional site occupation with the required charge being provided by a proton (not located) (see crystal structure determination). The compound is thus formulated as $Na_{5-x}H_x[Cu\{TeO_4(OH)_2\}_2]\cdot 16H_2O$ (x = 0.64) for the crystal examined. The structure of $K_5[Ag\{IO_5(OH)\}_2]\cdot 8H_2O$[9] also reported a larger (× 2) thermal parameter for one of the five K atoms. The co-ordination about each sodium ion is the expected approximate octahedron formed by the water molecules (Na ··· O. 2.30—2.61 Å) with the co-ordination about Na(2) being completed by oxygen atoms from the anion (see Figure 2). The NaO_6 octahedra form chains through the structure by face sharing [Na(1), Na(3)] and edge sharing [Na(1), Na(2‴); Na(2), Na(2″)].

Spectroscopic Studies.—The ions $[M\{TeO_4(OH)_2\}_2]^{5-}$ are diamagnetic[24] with the planar co-ordination about M confirmed by *X*-ray study of the copper complex (above). For these d^8 (S = 0) ions the *d*-orbital configuration is expected to be $d_{xy}{}^2 d_{xz}{}^2 d_{yz}{}^2 d_{z^2}{}^2 d_{x^2-y^2}{}^0$. Electronic spectra of these ions have been reported previously[25—27] although agreement between different workers is rather poor. Our spectra are in excellent agreement with the report of Balikungeri and Pelletier[27] with intense absorptions at 25 000 and 36 900 cm^{-1} (Cu) and 29 410 and 37 880 cm^{-1} (Ag) which can be assigned as $\pi(O) \longrightarrow M(d_{x^2-y^2})$ and $\sigma(O) \longrightarrow M(d_{x^2-y^2})$ respectively. The $[Au\{TeO_4(OH)_2\}_2]^{5-}$ exhibits only a single band at 40 800 cm^{-1}, the $\pi(O) \longrightarrow Au(d_{x^2-y^2})$ charge-transfer transition. No *d–d* transitions were observed, and presumably lie under the tails of the intense charge-transfer absorptions.

The i.r. spectra of these complexes[8,12] contain very broad absorptions with poorly defined maxima due to the large amounts of water present and extensive hydrogen bonding.

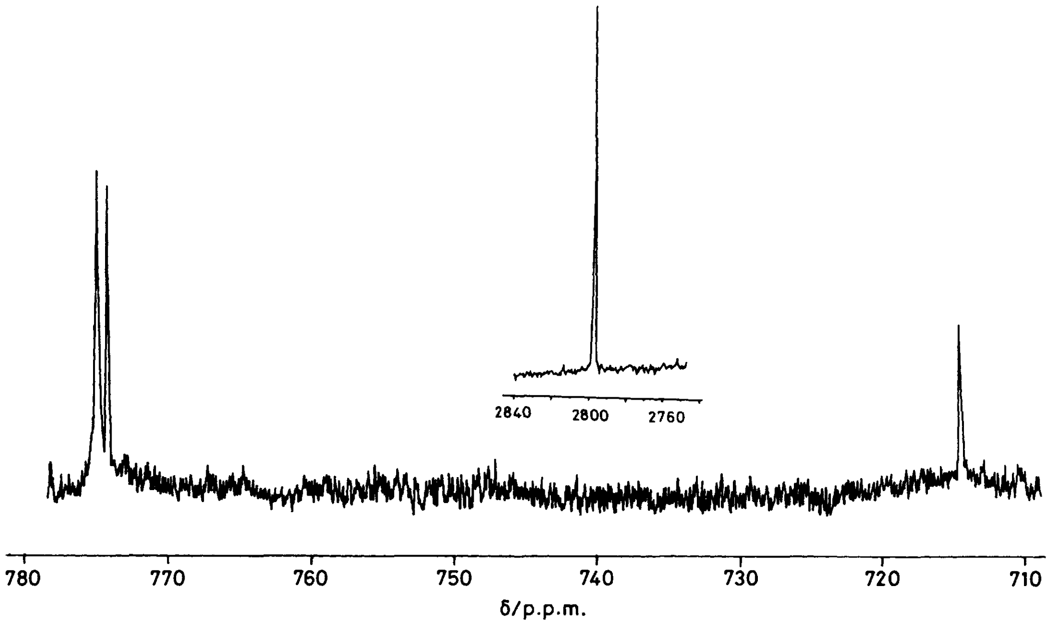

Figure 3. Tellurium-125 and (inset) ^{109}Ag n.m.r. spectra of the ion $[Ag\{TeO_4(OH)_2\}_2]^{5-}$ in water

Deuteriated analogues were obtained by dissolution of $Na_5[M\{TeO_4(OH)_2\}_2]\cdot nH_2O$ (M = Cu or Ag) in D_2O and evaporation *in vacuo*. A comparison of the i.r. spectra of the protiated and deuteriated forms allowed the identification of δ(TeOH) at *ca.* 1 100 cm^{-1}, which are replaced by δ(TeOD) *ca.* 850—950 cm^{-1} on deuteriation. For comparison, δ(TeOH) are found at 1 220—1 120 cm^{-1} for H_6TeO_6 and 1 200—1 140 cm^{-1} for $Na_2H_4TeO_6$.[28] These i.r. spectra provide clear evidence that the 'tellurate' ligands in the copper(III) and silver(III) complexes are protonated to some degree, consistent with the differing Te–O bond lengths observed in the *X*-ray study.

Telluric acid in D_2O has a ^{125}Te n.m.r. resonance at +713 p.p.m. (lit.,[29] 707 p.p.m.). The $[Cu\{TeO_4(OH)_2\}_2]^{5-}$ and $[Au\{TeO_4(OH)_2\}_2]^{5-}$ ions in D_2O containing a little 2 mol dm^{-3} NaOH have singlets at +774.5 and +753 p.p.m. respectively, while $[Ag\{TeO_4(OH)_2\}_2]^{5-}$ has a doublet at +774 p.p.m. [$^2J(^{107,109}\text{Ag}-^{125}\text{Te}) = 73$ Hz] (Figure 3). As a result of the relatively poor solubility of the complexes and the modest sensitivity of ^{125}Te n.m.r. spectroscopy ($I = \frac{1}{2}$; 7% abundance; receptivity relative to ^{1}H, 2.2×10^{-3}),[30] long accumulations were necessary to obtain good signal/noise ratios, typically 200—250 K transients, and during this time some decomposition occurred evident in the appearance of resonances due to tellurate ions and some precipitate. The ^{17}O n.m.r. spectrum of H_6TeO_6 was readily obtained (δ = 124; lit.,[31] 120 p.p.m.), but the poor solubility and the low abundance of ^{17}O frustrated attempts to record similar spectra for the complexes. The ^{109}Ag n.m.r. resonance of $[Ag\{TeO_4(OH)_2\}_2]^{5-}$ was found at +2 798 p.p.m. as a broad singlet with the ^{125}Te satellites just evident as ill defined shoulders. The ^{109}Ag resonance of $[Ag\{IO_5(OH)\}_2]^{5-}$ occurs at +2 802 p.p.m. These ^{109}Ag resonances appear to be the first reported for silver(III) species and may be compared with the typical range for silver(I) complexes, *ca.* +900 to −100 p.p.m. from the zero reference which is the Ag$^+$ ion in very dilute aqueous solution.[30] An attempt to observe the ^{63}Cu resonance in $[Cu\{TeO_4(OH)_2\}_2]^{5-}$ was unsuccessful, no signal being found within the range ±5 000 p.p.m. from $[Cu(MeCN)_4]^+$. Although ^{63}Cu ($I = \frac{3}{2}$, 69.1% abundant) is a relatively sensitive nucleus with a receptivity relative to the ^{1}H of 6.4×10^{-2}, it also has a moderate quadrupole moment -0.16×10^{-28} m^2.[30] As a consequence of the latter even small distortions from cubic symmetry produce broad lines,[32] and in the planar environment in the copper(III) complex the line is probably too broad to observe.

Acknowledgements

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