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The Crystal Structure of Tetraacetonitrile Silver(I) Perchlorate at 240 K

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The crystal structure of $[Ag(CH_3CN)_4]ClO_4$ has been determined from X-ray intensity data collected at 240 K with a CAD4 diffractometer. The space group is $Pn2_1a$ with $Z=12$; $a=24.50(1)$, $b=20.756(8)$ and $c=8.567(3)$ Å. the refinement converged to $R=0.048$. The structure is composed of discrete ions $[Ag(CH_3CN)_4]^+$ and ClO_4^-. The coordination geometry is close to tetrahedral with metal-nitrogen distances in the range 2.18(3)–2.33(2) Å. A geometric comparison is made with the isostructural Cu(I) compound, corresponding Ag(I)- and Cu(I)- pyridine compounds, and some related complexes with ligands containing the donor atoms S or P. From observed differences $d_{Ag-X}-d_{Cu-X'}$ X=N, S or P, the following order of softness for the donor atoms is proposed: N < S < P.

The crystal structure determination of $[Ag(CH_3CN)_4]ClO_4$ was undertaken as part of a research programme dealing with the coordination geometry of d^{10} ions. The observed coordination geometries are discussed in terms of donor–acceptor (hard – soft) properties [1] derived from thermodynamic parameters of complex formation in solution.[2] In a previous paper it was proposed that for isostructural compounds the difference in length between Ag–X and Cu–X bonds contains information about the covalency of these bonds.[3] One aim of the present project is to obtain information about the variation of the covalent capacity (softness) for various donor atoms from comparisons of pairs of isostructural compounds. $[Ag(CH_3CN)_4]ClO_4$ reported here is isostructural with $[Cu(CH_3CN)_4]ClO_4$.[4] This pair of isostructural compounds is compared with others containing the donor atoms N, S or P and an order of softness for these atoms is proposed.

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EXPERIMENTAL

$[Ag(CH_3CN)_4]ClO_4$ was prepared by dissolving silver(I) perchlorate in acetonitrile to a saturated solution. On cooling, colourless, needle-haped crystals were formed. The crystals lose acetonitrile rapidly at room temperature. Therefore the crystals used for the data collection had to be mounted on the goniometer at low temperature. The intensity data were collected at 240 K with the aid of a N_2 (g)-stream device. Laue class and systematic extinctions are consistent with space groups $Pnma$ and $Pn2_1a$. Cell dimensions were obtained from least-squares calculation of 22 θ-values determined as $\theta_{hkl}=(\omega_{hkl}-\omega_{\bar{h}\bar{k}\bar{l}})/2$ (Table 1).

A CAD4 diffractometer with $\omega_{\bar{h}\bar{k}\bar{l}}$ measured at negative θ-angle was used. The intensity data set was collected with the diffractometer using Zr-filtered Mo$K\alpha$-radiation. Two crystals were used, since the first one was destroyed through a failure of the low temperature device. During the data collection three standard reflexions were measured at regular intervals. For crystal No. 1 no variation in the intensities were observed, but for crystal No. 2 the control intensities decreased 20 % linearly with time (correction made). Information concerning the collection and reduction of the data is given in Table 1. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarisation and absorption effects, the latter by numerical integration ($\sigma_c(I)$ is based on counting statistics). Reflexions with $I<2.5\sigma_c(I)$ were considered insignificantly different from the background and excluded from all subsequent calculations.

The structure was refined using atomic parameters of the Cu-compound[4] as a starting set and assuming the space group $Pn2_1a$. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with empirical weights $w=[(\sigma_c^2/4|F_o|)^2+(0.005|F_o|)^2+4.0]^{-1}$. In the final refinement anisotropic temperature

Table 1. Crystal data, collection and reduction of intensity data and least-squares refinement.

Crystal No.	1	2
Crystal size (mm)	0.38×0.28×0.48	0.30×0.38×0.32
a (Å)		24.500(13)
b (Å)		20.756(8)
c (Å)		8.567(3)
V (Å^3)		4357
D_x (g cm^{-3})		1.70
Z		12
$\bar{\lambda}$ (Å)		0.7093
μ (cm^{-1})		15.5
Range of transmission factor		0.582–0.651
θ interval (°)		3.0–20.0
$\omega-2\theta$ scan width, $\Delta\omega$ (°)		0.75+0.5 tan θ
$\sigma_c(I)/I$ requested in a scan		0.030
Maximum recording time (s)		120
Number of reflexions measured	1042	2163
Number of reflexions with $I>2.5\sigma(I)$, m	752	1123
Number of parameters refined, n		367
$R=\Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|$		0.0477
$R_w=[\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$		0.0560
$S=[\Sigma w(\|F_o\|-\|F_c\|)^2/(m-n)]^{1/2}$		1.85

factor coefficients were applied on Ag, Cl, O and N. Scattering factors, with corrections for anomalous dispersion, were taken from the International Tables for X-Ray Crystallography.[5] Details of the refinement are given in Table 1. The final positional and isotropic thermal parameters averaged from the anisotropic values are given in Table 2 while Table 3 gives selected interatomic distances and angles. A list of structure factors and anisotropic thermal parameters may be obtained from the authors.

DESCRIPTION OF THE STRUCTURE

The compound is composed of discrete ions $[Ag(CH_3CN)_4]^+$ and ClO_4^-. The crystal packing is shown in Fig. 1. The asymmetric unit (Fig. 2) comprises three Ag^+-complexes and three ClO_4^- ions, which alternate along the c-axis in such a way that the three Ag and the three Cl are approximately related by a three-fold pseudoaxis not obeyed by the other atoms. The cation as well as the anion have a slightly distorted tetrahedral symmetry (Table 3). The Cl–O distances are in the range 1.34(2)–1.49(3) Å, which is about the same as observed in the isostructural Cu(I)-compound.[4] The Cl–O bonds are fairly strong and the bond lengths should not be much affected by packing forces. The large range observed is therefore most probably artifacts due to thermal motion of the perchlorate ion. A similar large range is observed for the Ag–N distances, 2.18(3)–2.33(2) Å. However, in this case the

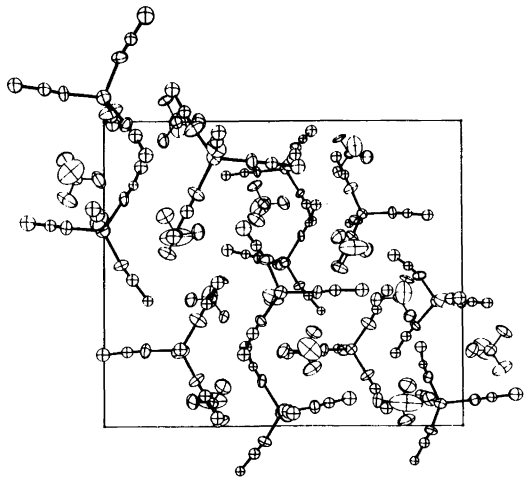

Fig. 1. Packing of $[Ag(CH_3CN)_4]ClO_4$ viewed along c. The b-axis is vertical and the a-axis is horizontal.

Table 2. Atomic coordinates and isotropic thermal parameters with e.s.d's. For Ag, Cl, N and O B is calculated from anisotropic temperature factors ($\exp-(\beta_{11}h^2+\beta_{22}k^2+\ldots)$) using the expression $B=\frac{4}{3}\Sigma\Sigma\beta_{ij}a_ia_j$.

	x	y	z	B(Å)
Ag(1)	0.2128(1)	0.2500(0)	0.8067(2)	4.48(5)
Ag(2)	0.4616(1)	0.0662(1)	0.7120(2)	4.55(7)
Ag(3)	0.4581(1)	0.4139(2)	0.7611(2)	4.62(7)
Cl(1)	0.5444(2)	0.2465(4)	0.2647(7)	4.5(2)
Cl(2)	0.2975(3)	0.0828(3)	0.2225(7)	3.7(2)
Cl(3)	0.2959(3)	0.4116(4)	0.2184(6)	3.8(2)
N(11)	0.1262(7)	0.2480(13)	0.7178(20)	5.2(6)
N(12)	0.2517(11)	0.1628(12)	0.7177(27)	5.4(8)
N(13)	0.2559(12)	0.3364(12)	0.7084(27)	6.0(9)
N(14)	0.2117(9)	0.2462(15)	1.0714(22)	5.7(7)
N(21)	0.4165(8)	0.1574(11)	0.6200(21)	4.0(6)
N(22)	0.4232(9)	−0.0212(9)	0.6138(23)	4.2(6)
N(23)	0.5492(9)	0.0802(10)	0.6230(23)	4.9(7)
N(24)	0.4603(11)	0.0746(14)	0.9785(27)	7.1(9)
N(31)	0.4195(9)	0.5040(10)	0.8650(23)	4.6(7)
N(32)	0.4059(8)	0.3309(10)	0.8575(25)	4.2(6)
N(33)	0.5433(8)	0.4117(11)	0.8567(20)	4.2(5)
N(34)	0.4506(12)	0.4082(15)	0.5019(24)	8.5(10)
C(11)	0.0806(9)	0.2440(14)	0.7054(22)	3.6(4)
C(12)	0.0200(9)	0.2366(15)	0.6854(27)	5.2(6)
C(13)	0.2724(12)	0.1168(14)	0.7007(32)	4.3(6)
C(14)	0.3030(12)	0.0516(15)	0.6802(33)	5.3(7)
C(15)	0.2772(11)	0.3840(13)	0.6886(30)	3.6(5)
C(16)	0.3049(12)	0.4471(14)	0.6598(32)	5.1(6)
C(17)	0.2125(9)	0.2507(16)	1.1976(28)	3.5(4)
C(18)	0.2117(9)	0.2519(17)	1.3635(23)	3.9(5)
C(21)	0.3962(9)	0.1996(11)	0.5593(24)	2.3(4)
C(22)	0.3798(9)	0.2577(14)	0.4708(25)	4.6(6)
C(23)	0.3985(11)	−0.0593(13)	0.5619(28)	3.8(6)
C(24)	0.3638(10)	−0.1148(11)	0.5005(26)	2.8(5)
C(25)	0.5890(11)	0.0903(11)	0.5652(27)	3.5(5)
C(26)	0.6461(14)	0.1020(16)	0.4925(35)	6.2(8)
C(27)	0.4606(11)	0.0821(14)	1.1027(35)	4.6(6)
C(28)	0.4624(12)	0.0832(13)	1.2698(27)	4.5(6)
C(31)	0.3930(10)	0.5407(12)	0.9299(28)	3.3(5)
C(32)	0.3600(14)	0.5829(16)	1.0292(36)	6.1(8)
C(33)	0.3839(11)	0.2947(13)	0.9202(29)	4.0(5)
C(34)	0.3603(10)	0.2366(15)	1.0030(26)	4.4(6)
C(35)	0.5817(10)	0.4146(12)	0.9192(24)	3.5(5)
C(36)	0.6389(11)	0.4129(16)	1.0097(28)	4.6(6)
C(37)	0.4539(11)	0.4119(17)	0.3754(34)	4.9(6)
C(38)	0.4552(12)	0.4093(17)	0.2007(30)	5.4(6)
O(11)	0.4890(7)	0.2462(14)	0.2122(25)	8.7(7)
O(12)	0.5677(13)	0.1893(13)	0.2052(33)	10.3(11)
O(13)	0.5726(10)	0.3047(11)	0.2042(32)	8.5(9)
O(14)	0.5483(11)	0.2502(18)	0.4203(20)	12.7(11)
O(21)	0.2439(10)	0.0890(11)	0.2829(31)	8.9(9)
O(22)	0.3199(11)	0.0268(10)	0.2788(28)	8.3(9)
O(23)	0.3245(13)	0.1352(13)	0.2886(34)	10.3(11)
O(24)	0.2976(17)	0.0865(13)	0.0656(27)	15.9(17)
O(31)	0.2408(8)	0.4073(12)	0.2780(23)	6.7(7)
O(32)	0.3288(9)	0.3543(11)	0.2582(24)	6.7(8)
O(33)	0.3223(10)	0.4703(8)	0.2662(23)	6.0(7)
O(34)	0.2930(9)	0.4216(15)	0.0642(18)	9.4(10)

Table 3. Selected interatomic distances (Å) and angles (°) with e.s.d.'s.

(a) The coordination polyhedra

		N(11)–Ag(1)–N(12)	106.1(10)
Ag(1)–N(11)	2.26(2)	N(11)–Ag(1)–N(13)	109.3(9)
Ag(1)–N(12)	2.18(3)	N(11)–Ag(1)–N(14)	109.0(7)
Ag(1)–N(13)	2.25(3)	N(12)–Ag(1)–N(13)	109.0(10)
Ag(1)–N(14)	2.27(2)	N(12)–Ag(1)–N(14)	109.0(10)
		N(13)–Ag(1)–N(14)	114.1(10)
		N(21)–Ag(2)–N(22)	109.6(7)
Ag(2)–N(21)	2.33(2)	N(21)–Ag(2)–N(23)	103.2(7)
Ag(2)–N(22)	2.21(2)	N(21)–Ag(2)–N(24)	105.6(9)
Ag(2)–N(23)	2.30(2)	N(22)–Ag(2)–N(23)	112.1(8)
Ag(2)–N(24)	2.29(2)	N(22)–Ag(2)–N(24)	115.9(9)
		N(23)–Ag(2)–N(24)	109.5(8)
		N(31)–Ag(3)–N(32)	104.1(7)
Ag(3)–N(31)	2.28(2)	N(31)–Ag(3)–N(33)	105.2(8)
Ag(3)–N(32)	2.30(2)	N(31)–Ag(3)–N(34)	113.5(10)
Ag(3)–N(33)	2.24(2)	N(32)–Ag(3)–N(33)	111.7(7)
Ag(3)–N(34)	2.23(2)	N(32)–Ag(3)–N(34)	105.7(10)
		N(33)–Ag(3)–N(34)	116.1(9)

(b) The acetonitrile molecules

N(11)–C(11)	1.13(3)	Ag(1)–N(11)–C(11)	165(2)
C(11)–C(12)	1.50(3)	N(11)–C(11)–C(12)	178(3)
N(12)–C(13)	1.09(4)	Ag(1)–N(12)–C(13)	167(2)
C(13)–C(14)	1.56(4)	N(12)–C(13)–C(14)	178(3)
N(13)–C(15)	1.13(4)	Ag(1)–N(13)–C(15)	166(2)
C(15)–C(16)	1.50(4)	N(13)–C(15)–C(16)	179(3)
N(14)–C(17)	1.09(3)	Ag(1)–N(14)–C(17)	173(3)
C(17)–C(18)	1.42(3)	N(14)–C(17)–C(18)	176(4)
N(21)–C(21)	1.13(3)	Ag(2)–N(21)–C(21)	172(2)
C(21)–C(22)	1.48(4)	N(21)–C(21)–C(22)	170(2)
N(22)–C(23)	1.09(3)	Ag(2)–N(22)–C(23)	171(2)
C(23)–C(24)	1.53(4)	N(22)–C(23)–C(24)	176(3)
N(23)–C(25)	1.11(3)	Ag(2)–N(23)–C(25)	172(2)
C(25)–C(26)	1.55(4)	N(23)–C(25)–C(26)	177(3)
N(24)–C(27)	1.08(4)	Ag(2)–N(24)–C(27)	176(3)
C(27)–C(28)	1.43(4)	N(24)–C(27)–C(28)	172(3)
N(31)–C(31)	1.15(3)	Ag(3)–N(31)–C(31)	166(2)
C(31)–C(32)	1.46(4)	N(31)–C(31)–C(32)	173(3)
N(32)–C(33)	1.07(3)	Ag(3)–N(32)–C(33)	171(2)
C(33)–C(34)	1.51(4)	N(32)–C(33)–C(34)	171(3)
N(33)–C(35)	1.08(3)	Ag(3)–N(33)–C(35)	171(2)
C(35)–C(36)	1.60(4)	N(33)–C(35)–C(36)	175(3)
N(34)–C(37)	1.09(4)	Ag(3)–N(34)–C(37)	168(3)
C(37)–C(38)	1.50(4)	N(34)–C(37)–C(38)	173(4)

(c) The perchlorate ions

		O(11)–Cl(1)–O(12)	105(2)
Cl(1)–O(11)	1.43(2)	O(11)–Cl(1)–O(13)	110(2)
Cl(1)–O(12)	1.41(3)	O(11)–Cl(1)–O(14)	112(1)
Cl(1)–O(13)	1.49(3)	O(12)–Cl(1)–O(13)	112(2)
Cl(1)–O(14)	1.34(2)	O(12)–Cl(1)–O(14)	112(2)
		O(13)–Cl(1)–O(14)	105(2)
		O(21)–Cl(2)–O(22)	109(2)

Cl(2)–O(21)	1.42(3)	O(21)–Cl(2)–O(23)	103(2)
Cl(2)–O(22)	1.37(2)	O(21)–Cl(2)–O(24)	111(2)
Cl(2)–O(23)	1.39(3)	O(22)–Cl(2)–O(23)	109(2)
Cl(2)–O(24)	1.35(2)	O(22)–Cl(2)–O(24)	113(2)
		O(23)–Cl(2)–O(24)	111(2)
		O(31)–Cl(3)–O(32)	112(1)
Cl(3)–O(31)	1.45(2)	O(31)–Cl(3)–O(33)	112(1)
Cl(3)–O(32)	1.48(2)	O(31)–Cl(3)–O(34)	108(1)
Cl(3)–O(33)	1.44(2)	O(32)–Cl(3)–O(33)	112(1)
Cl(3)–O(34)	1.34(2)	O(32)–Cl(3)–O(34)	112(2)
		O(33)–Cl(3)–O(34)	100(2)

observation may be of chemical significance, as discussed below, since the range observed in the isostructural Cu(I) compound is much smaller, 1.95(1)–2.02(1) Å.[4] The acetonitrile molecules are linear (Table 3) with Ag–N–C angles in the range 165(2)–176(3)°. The average C–C and C–N bond distances are 1.50(5) and 1.10(3) Å, respectively.

DISCUSSION

The crystalline state represents the atomic arrangement of minimum energy. The energy minimum is a compromise between intra and intermolecular forces. In a complex $[M(CH_3CN)_4]^+$ a more ideal coordination geometry is expected for strong donor–acceptor interactions than for weak ones.

The range observed for the Ag–N distances, 2.18–2.33 Å with an average of 2.26(4) Å, is larger than expected for a normal distribution of errors. In the isostructural Cu(I) compound the Cu–N distances are in the range 1.95–2.02 Å with an average of 1.99(2) Å.[4] In the Cu-compound the interval is thus much smaller than in the Ag-compound but somewhat larger than expected for a normal distribution of errors. The distribution of observed M–N distances for these compounds may be due not only to experimental errors, but also to the interplay between crystal packing and donor–acceptor forces. On the assumption that the strength of the packing forces is about the same in the two compounds it may be concluded that the Cu–N bonds are stronger than the Ag–N bonds. This is in agreement with the order of solvation enthalpies, which are −679 and −529 kJ mol^{-1} for Cu^+ and Ag^+, respectively.[6]

The acetonitrile compounds discussed above may be compared with the corresponding pyridine complexes, $[M(C_5H_5N)_4]ClO_4$, M=Cu, Ag,[3] where the four M–N bonds are symmetrically equivalent. The distances are 2.046(4) and 2.322(3) Å for the Cu(I) and Ag(I) compound, respectively. Both the Ag–N and the Cu–N distances are 0.06 Å shorter in the acetonitrile than in the pyridine complexes. This cannot be the result of stronger bonds to acetonitrile than to pyridine, since the solvation enthalpies are 55

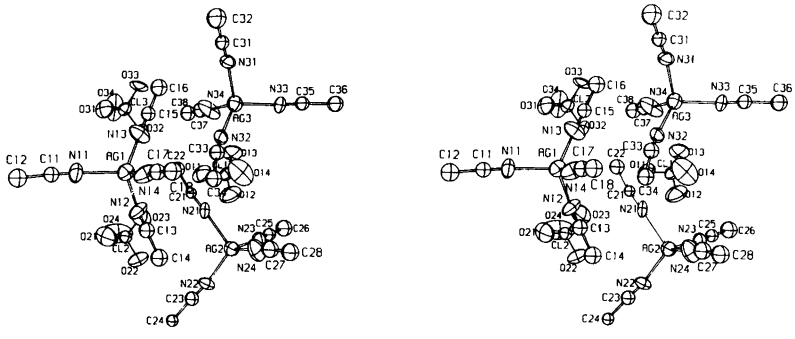

Fig. 2. Stereoscopic view of the asymmetric unit.

Table 4. Distances, d_{M-X}(Å), and differences, $\Delta = d_{Ag-X} - d_{Cu-X}$ (Å), for some compounds containing complexes with donor atoms N, S or P.

	d_{Ag-N}	d_{Cu-N}	Δ	Ref.
$[M(CH_3CN)_4]ClO_4$	2.18(3)–2.33(2)	1.95(1)–2.02(1)	0.27(5)	This work
$[M(C_5H_5N)_4]ClO_4$	2.322(3)	2.046(4)	0.276(5)	3
$[MIC_5H_{11}N]_4$	2.329(15)	2.052(7)	0.277(17)	7 and 8
	d_{Ag-S}	d_{Cu-S}		
$M(SCN_2H_4)_3ClO_4$	2.663(2)–2.684(2)[a]	2.395(4)–2.460(4)[a]	0.25(3)	9 and 10
	2.524(2)–2.570(2)	2.321(4)–2.326(5)	0.22(4)	
	d_{Ag-P}	d_{Cu-P}		
$[PEt_3MCl]_4$	2.390(2)	2.176(2)	0.214(3)	11 and 12
$[PEt_3MBr]_4$	2.402(5)	2.199(2)	0.203(6)	11 and 12
$[PEt_3MI]_4$	2.438(2)	2.254(3)	0.188(4)	13 and 14

[a] Bridging bonds.

(Cu^+) and 65 (Ag^+) kJ mol^{-1} more negative for pyridine as compared to acetonitrile.[6] The shorter bond lengths in acetonitrile are most probably the result of a smaller (0.06 Å) coordination radius for N in an acetonitrile than in a pyridine molecule.

It has been shown previously that differences in bond lengths may, in special cases, be used to estimate differences in covalency between bonds:[3]

$$\Delta = d_{Ag-X} - d_{Cu-X} = r_{Ag} - r_{Cu} - (\sigma_{cov,Ag-X} - \sigma_{cov,Cu-X})$$

Here r_M is the ionic radius and $\sigma_{cov,\ M-X}$ is a function of the covalency of the M–X bond. Thermodynamic measurements in solution indicate that the covalent bonding capacity is larger for Ag(I) than for Cu(I)[2], *i.e.* $\sigma_{cov,\ Ag-X} > \sigma_{cov,\ Cu-X}$. If X is an ideal hard donor atom, both bonds are purely ionic and Δ is the difference in ionic radius for the metal ions. For softer donor atoms the difference $\sigma_{cov,\ Ag-X} - \sigma_{cov,\ Cu-X}$ should increase with the softness of X. The quantity Δ may thus be used as a measure of softness for donor atoms.

Table 4 gives Δ for pairs of Cu and Ag compounds containing ligands with donor atoms N, S and P. The cluster compounds $[MIC_5H_{11}N]_4$, M=Cu and Ag contain a M_4I_4 core. Each metal atom is also coordinated to one nitrogen atom, resulting in a tetrahedral arrangement around M. Tris(thiourea)copper(I) perchlorate and the corresponding Ag-compound consist of binuclear complexes with two bridging sulfur atoms and the remaining sulfurs terminal. The metal atoms are tetrahedrally surrounded by four sulfur atoms. The phosphorus compounds are clusters analogous to those described above. As expected the Δ values indicate the order of softness, P>S>N. Furthermore, it may be concluded that the difference in ionic radius between Ag^+ and Cu^+ is larger than 0.28 Å for tetrahedral coordination geometry.

The values of Δ for the acetonitrile and the pyridine complexes are not significantly different. This method is thus in this case, not sensitive enough to resolve an eventual difference in covalent bonding capacity between nitrogen in acetonitrile and pyridine.

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