complex. In the case of the attempted synthesis of the *p*-tolyl derivative of $Mo_2(CO)_6(IAE)$, it appears $Mo_2(CO)_6(IAE)$ is formed but rapidly reconverts back into $Mo(CO)_4(DAB)$. Thus $Mo(CO)_4(DAB)$ would appear unreactive.

A striking feature of IAE formation is that at present good yields are only obtained for second-row transition metals. However, complexes with "σ,π-coordinated" DAB ligands, which is a prerequisite for IAE formation, are also known for first- and third-row transition metals. In these complexes IAE formation has as yet not been observed, although the analogous dimerization of ethyl *N*-(α-methylbenzyl)iminoacetate did occur on a $Fe_2(CO)_6$ fragment.[35] Whether IAE formation is restricted to second-row transition metals, or that under suitable conditions the first- and third-row elements also form IAE complexes, is a subject of further investigation.

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Registry No. $Ru_2(CO)_6$(*t*-Bu, H), 74552-68-4; $Ru_2(CO)_6$(*i*-Pr, H), 74552-69-5; $Ru_2(CO)_6$(cHx, H), 74552-70-8; $Ru_2(CO)_6$(*i*-Pr, H/CH_3), 74552-71-9; $Ru_2(CO)_5$(*t*-Bu, H), 72918-61-7; $Ru_2(CO)_5$(*i*-Pr, H), 72918-60-6; $Ru_2(CO)_5$(cHx, H), 74562-46-2; $Ru_2(CO)_5$(*i*-Pr, H/CH_3), 74562-47-3; $Ru_2(CO)_4$(*i*-Pr, H), 72918-62-8; $Ru_2(CO)_4$(cHx, H), 74562-48-4; $Ru_2(CO)_4$(*i*-Pr, H)$_2$, 74552-72-0; $Ru_2(CO)_4$(cHx, H)$_2$, 74562-49-5; $Ru_2(CO)_4$(*p*-tol, H)$_2$, 74552-73-1; $Fe_2(CO)_6$(*t*-Bu, H), 65045-67-2; $Fe_2(CO)_6$(*i*-Pr, H), 74552-74-2; $Fe_2(CO)_6$(*i*-Pr, H/CH_3), 74552-75-3; $Fe_2(CO)_6$(*p*-tol, H), 74552-76-4; $Ru_3(CO)_{12}$, 15243-33-1; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of thermal parameters, elemental analyses, and structure factors and the observed and simulated mass spectra of $Ru_2(CO)_6$[glyoxal bis(cyclohexylimine)] (16 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Molecular Structure of Tetraethylammonium Pentakis(isothiocyanato)bis(2,2′-bipyridine)uranate(IV)

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The synthesis of tetraethylammonium pentakis(isothiocyanato)bis(2,2′-bipyridine)uranate(IV) has been accomplished, and it was characterized by classical physical methods. The crystal and molecular structure was determined from single-crystal X-ray data collected by the $\theta-2\theta$ technique on an automated diffractometer. The compound consists of pentakis(isothiocyanato)bis (2,2′-bipyridine)uranate(IV) anions and disordered tetraethylammonium cations. Uranium is bound to nine nitrogen atoms in a highly distorted monocapped square antiprism in which one bipyridine occupies a position bridging the cap and the near square while the other bipyridine spans the opposite edge of the far square. Distortion from the ideal geometry is caused by the small ligand bite of the bipyridine ligand. An alternative description of the coordination geometry is derived from the seven-coordinate pentagonal bipyramid in which each bipyridine ligand is assumed to occupy an axial position with the five thiocyanato ligands forming the pentagonal girdle. The U–N bond distances vary from 2.35 to 2.47 Å for the thiocyanato ligands and from 2.61 to 2.65 Å for the bipyridine ligands. The structure was solved by standard heavy-atom techniques and refined by large-block matrix least squares to a final *R* value of 0.083 for 3878 indpendent observed reflections. The compound crystallized in the monoclinic space group $P2_1/c$, $Z = 4$, with lattice parameters $a = 14.427$ (10) Å, $b = 18.612$ (17) Å, $c = 15.710$ (10) Å, and $\beta = 105.17$ (7)°, $\rho_{obsd} = 1.57$ g cm^{-3} ($\rho_{calcd} = 1.58$ g cm^{-3}).

Introduction

Coordination numbers greater than 8, with the exception of that for $[ReH_9]^{2-}$,[1] are largely limited to the lanthanides and actinides. This is due to the greater metal size required for more than eight ligands. There are a number of examples of metals exhibiting coordination number 9; the majority of these compounds are polymeric rather than monomeric. The title compound $[Et_4N]^+[U(NCS)_5(bpy)_2]^-$, is one of a small number of nine-coordinate uranium compounds,[2,3] and this compound is unique in that it is the first monomeric nine-coordinate compound characterized to be of the type $M(AA)_2L_5$ (AA = bidentate ligand, L = monodentate ligand). Some other examples of compounds displaying nine-coordination are $[M(OH_2)_9]^{3+}$ (M = Pr, Yb,[4] and Ho[5]), $Er(OAc)_3 \cdot 4H_2O$,[6] $Th(trop)_4(OH_2)$,[7] and $CeCl_3 \cdot 7H_2O$.[8]

The coordination polyhedra of nine-coordinate structures are invariably described in terms of either a monocapped square antiprism (MSAP) or a tricapped trigonal prism (TTP). "Points on a sphere" repulsive calculations[9] show the TTP to be the most favored coordination geometry. However, the difference in energy between the TTP and the MSAP is less than 0.1% of the total energy of either form. Various means of assigning the correct coordination polyhedron to a nine-coordinate structure have been proposed.[9–12] Identification is achieved either by examination of the dihedral angles formed by triangular faces or by comparison to the ideal polyhedron by means of a least-squares-fit calculation.[11] In the instance of a structure strongly distorted by multidentate ligands, this second method is the best since the dihedral angles will vary wildly, and unpredictably, from the ideal values for either the

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TTP or the MSAP or any pathway between the two ideals.

Experimental Section

Due to the sensitivity of starting materials to hydrolysis, it was necessary to exclude water during preparation, handling, and storage. In order to maintain these conditions, we used standard inert-atmosphere and vacuum techniques.

Materials. $(Et_4N)_4U(NCS)_8$ was prepared by previously published methods.[13] 2,2′-Bipyridyl (bpy) was obtained from Aldrich Chemical Co., recrystallized from 95% ethanol, and dried in vacuo before use. Analytical reagent grade acetonitrile, obtained from Mallinckrodt Chemical Works, was dried and outgassed over phosphorus pentoxide and stored over Linde type 4A molecular sieves.

Preparation and Characterization of $[Et_4N]^+[U(NCS)_5(C_{10}H_{10}N_2)_2]^-$. A 1.5-g sample of $(Et_4N)_4U(NCS)_8$ (0.001 23 mol) and 2.21 g of 2,2′-bipyridyl (0.014 mol) were placed into one side of an inverted U-shaped crystallization vessel. Approximately 50 mL of acetonitrile was vacuum distilled onto the reactants, and the vessel was then sealed off. The solution was allowed to stand several days with periodic stirring, and then the solvent was slowly distilled over to the other side of the vessel by directing a small fan at the side containing the reaction mixture. Small green crystals, suitable for X-ray work, slowly formed within 1 week. The remaining solution was then decanted from the crystals. The crystals are stable to hydrolysis in air. Anal. Calcd for $[(C_2H_5)_4N]^+[U(NCS)_5(C_{10}H_{10}N_2)_2]^-$: C, 40.82; N, 14.42; H, 3.74. Found: C, 40.46; N, 14.18; H, 3.78. NMR (CD_3CN solution 35 °C): 1.40 (t of t, CH_3) and 3.46 ppm (q, CH_2) relative to an internal reference of tetramethylsilane. IR (200–1400 cm^{-1}, Nujol mull; 1400–4000 cm^{-1}, Fluorolube mull): 2050 s (ν_{CN}); 1603 m (bpy); 1578 w, 1478 m, 1440 m, 1317 m, 1283 w, 1242 w, 1223 w, 1180 m, 1170 sh, 1068 m, 1012 s, 1005 sh, 977 w, 924 m (CS); 899 w, 771 s, 739 s (bpy); 726 vw, 652 w, 643 m, 625 m, 491 s (δ_{NCS}); 420 m (bpy); 231 s (UN).

Crystal Data and Collection. Because of the stability of the crystals to hydrolysis, a suitable crystal of approximate dimensions 0.19 × 0.15 × 0.14 mm was mounted in a random orientation on the end of a glass fiber. On the basis of precession photographs, the lattice was assigned to the monoclinic system. The systematic extinctions of $0k0$ for k odd and $h0l$ for l odd are uniquely consistent with the centrosymmetric space group $P2_1/c$ (C_{2h}^5).[14] Least-squares analysis of 15 reflections ($2.97 \leq 2\theta \leq 13.54°$) measured with a Syntex P$\bar{1}$ autodiffractometer at room temperature yielded the lattice parameters $a = 14.427$ Å, $b = 18.612$ (17) Å, $c = 15.710$ (10) Å and $\beta = 105.17$ (7)°, which for $Z = 4$ gives $\rho_{calcd} = 1.58$ g cm^{-3} ($\rho_{obsd} = 1.57$ g cm^{-3}, by flotation in CCl_4–$C_2H_2Br_4$ solution). The faces and distances from a central point of the irregularly shaped crystal used for data collection were as follows: (010), 0.10 mm; $(0\bar{1}0)$, 0.10 mm; (001), 0.09 mm; $(00\bar{1})$, 0.09 mm; $(11\bar{1})$, 0.07 mm; $(\bar{1}\bar{1}1)$, 0.07 mm; $(\bar{1}11)$, 0.07 mm; $(1\bar{1}\bar{1})$, 0.07 mm. Intensity data were collected with the crystal mounted on a glass fiber roughly parallel to the $(11\bar{1})$ face. Examination of ω scans for a number of low-order reflections suggested the crystal was single and was of good quality.

Diffraction intensities were measured for 10 092 independent reflections within the angular range $4° \leq 2\theta \leq 55°$ with monochromated Mo$K\alpha$ ($\lambda = 0.710\,69$ Å) radiation by using θ–2θ scans of 1°/min. The base scan range was 0.7° above and below $K\alpha_1$ and $K\alpha_2$, respectively, and background measurements lasting 0.10 of the scan time were made at each end of the scan. Periodic monitoring of four reflections was used to correct for intensity variations throughout the data collection. The largest 3878 independently observed reflections were used in all subsequent least-squares refinement processes. The usual Lorentz and polarization corrections for monochromated radiation[15] were applied and analytical absorption corrections[16] were made for a linear absorption coefficient of 40.6 cm^{-1}.

Structure Solution and Refinement. The atomic scattering factors for U^0, S^0, N^0, C^0, and H^0 from published tables were used with real and imaginary anomalous dispersion correction[17] applied for U and S. The function minimized during all least-squares refinement processes was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$. Residuals used below are defined as

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

A three-dimensional Patterson synthesis[18] provided the location of the uranium atoms in the unit cell. A Fourier synthesis using the uranium atom position indicated the positions of all nonhydrogen atoms in the anion complex. These 40 atoms were refined isotropically to give a standard residual of $R = 0.122$ and a weighted residual of $R_w = 0.131$. The Fourier synthesis following this refinement did not indicate the atom positions in the tetraethylammonium ion other than that of the nitrogen atom. Uranium and sulfur positions were refined anisotropically, resulting in the residuals $R = 0.086$ and $R_w = 0.123$. The Fourier synthesis again did not clearly indicate the carbon atom positions in the tetraethylammonium ion. Anisotropic refinement of all 40 known atom positions gave residuals $R = 0.069$ and $R_w = 0.115$. Although the position of the nitrogen atom of the tetraethylammonium ion could be found in all cases, it was apparent that the degree of disorder in the carbon atom positions precluded the possibility of defining all these positions and their occupancies. Therefore, a spherically symmetric scattering factor was calculated[19] for the tetraethylammonium ion on the basis of published atomic positions.[20] This scattering factor was then applied to the nitrogen atom position as atom "T" and refined isotropically. This resulted in residuals $R = 0.094$ and $R_w = 0.078$. (The increase in the unweighted residual after this refinement was deemed unimportant in light of the large decrease in the weighted R value, R_w, which is the proper indicator of the quality of the refinement.) At this point, hydrogen atoms on the bipyridine ligands were placed at idealized positions, each with an isotropic temperature factor of $U = 0.05$ Å^2. Three final cycles of large-block least-squares refinement, fixing all hydrogen parameters, resulted in the residuals $R = 0.083$ and $R_w = 0.068$. On the final refinement cycle, no parameter shift to esd ratio was greater than 0.07. A final difference Fourier synthesis showed one peak of 4.02 e/Å^3 in the region of the uranium atom. Numerous scattered peaks of approximately 1.0 e/Å^3 appeared in the region containing the tetraethylammonium ion but could not be rationalized in terms of a set of multiply disordered ethyl positions. Listings of final values of $|F_o|$ and $|F_c|$ (in electrons × 5) and phases of the reflections used in the refinement of the structure are available. (See paragraph at end of paper regarding supplementary material.)

Results and Discussion

A green, air-stable crystalline compound, formulated as $[Et_4N]^+[U(NCS)_5(bpy)_2]^-$, was obtained from an acetonitrile solution of $[Et_4N]_4[U(NCS)_8]$ and approximately fourfold excess of 2,2′-bipyridyl. It exhibits typical resonances for a tetraethylammonium ion (1.40 ppm, t of t; 3.46 ppm, q) in CD_3CN solutions at 35 °C. The infrared spectrum shows absorptions typical of coordinated bipyridine and thiocyanato ligands.

Final atomic coördinates and anisotropic thermal parameters for the nonhydrogen atoms are presented in Table I along with the estimated standard deviations derived from the least-squares analysis. Atomic coordinates for the hydrogen atoms are given in Table II. Figure 1 shows the essential features of the $[U(NCS)_5(bpy)_2]^-$ anion. Each atom is represented by an ellipsoid consistent with the anisotropic thermal parameters in Table I, and the atoms are labeled consistently with atom names as given in Table I. A stereoscopic view of the molecular packing and unit-cell contents for $[Et_4N]^+[U(NCS)_5(bpy)_2]^-$ is shown in Figure 2. Bond lengths and spherical angles within the coordination polyhedron are given

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Table I. Fractional Coordinates[a] ($\times 10^4$) and Thermal Parameters[b] ($\times 10^3$) for All Nonhydrogen Atoms in $[Et_4N]^+[U(NCS)_5(bpy)_2]^-$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	1590 (1)	764 (1)	2760 (1)	57.7 (5)	61.3 (5)	65.5 (5)	−3.4 (7)	20.4 (4)	3.0 (7)
N(A)	1244 (11)	−228 (8)	1504 (11)	80 (13)	55 (12)	79 (13)	0 (11)	28 (11)	8 (10)
C(A1)	1051 (13)	−907 (10)	1701 (12)	89 (16)	46 (16)	67 (15)	−24 (12)	22 (12)	−15 (13)
C(A2)	983 (15)	−1448 (11)	1163 (15)	84 (18)	74 (18)	84 (19)	−3 (15)	2 (15)	−12 (14)
C(A3)	1098 (16)	−1274 (13)	309 (17)	79 (19)	90 (22)	135 (25)	−53 (19)	−15 (18)	26 (16)
C(A4)	1246 (17)	−596 (12)	99 (14)	158 (25)	68 (21)	72 (17)	9 (15)	42 (16)	−12 (17)
C(A5)	1313 (15)	−69 (11)	700 (13)	104 (19)	53 (15)	55 (16)	−9 (13)	33 (14)	−9 (14)
N(B)	1430 (11)	1173 (9)	1139 (11)	71 (13)	70 (13)	89 (15)	4 (11)	17 (11)	−3 (11)
C(B1)	1455 (17)	1861 (11)	883 (16)	135 (23)	51 (16)	102 (21)	10 (15)	34 (18)	22 (16)
C(B2)	1559 (17)	2091 (13)	103 (17)	134 (24)	109 (23)	93 (22)	61 (19)	32 (19)	3 (19)
C(B3)	1618 (17)	1607 (16)	−525 (16)	116 (23)	149 (27)	86 (21)	13 (20)	43 (18)	−8 (21)
C(B4)	1533 (17)	868 (14)	−338 (14)	142 (23)	111 (22)	80 (18)	7 (19)	36 (16)	4 (20)
C(B5)	1429 (13)	651 (12)	515 (13)	71 (15)	90 (20)	66 (16)	2 (16)	26 (13)	3 (15)
N(C)	999 (12)	1041 (8)	4171 (10)	73 (13)	82 (14)	70 (12)	−14 (11)	29 (11)	−11 (11)
C(C1)	99 (16)	1156 (12)	4135 (15)	69 (17)	124 (21)	107 (21)	−27 (17)	31 (16)	12 (16)
C(C2)	−265 (17)	1137 (14)	4909 (21)	86 (21)	138 (25)	180 (31)	−21 (24)	90 (22)	−17 (18)
C(C3)	371 (25)	1032 (15)	5714 (18)	202 (37)	132 (29)	120 (27)	20 (22)	53 (25)	29 (27)
C(C4)	1288 (19)	907 (14)	5754 (15)	134 (25)	150 (27)	91 (20)	42 (20)	41 (18)	71 (22)
C(C5)	1588 (15)	919 (10)	4988 (14)	82 (17)	59 (17)	78 (17)	−17 (14)	32 (14)	2 (14)
N(D)	2870 (11)	884 (8)	4282 (10)	67 (12)	73 (13)	80 (13)	−6 (12)	23 (10)	5 (12)
C(D1)	3784 (16)	874 (12)	4324 (13)	76 (17)	111 (20)	73 (16)	−15 (17)	4 (13)	−19 (19)
C(D2)	4493 (15)	826 (13)	5098 (17)	89 (19)	96 (19)	126 (23)	−37 (23)	6 (17)	12 (18)
C(D3)	4238 (18)	822 (15)	5845 (16)	98 (21)	143 (24)	94 (20)	−46 (22)	−27 (17)	−12 (23)
C(D4)	3311 (18)	812 (14)	5852 (13)	125 (22)	135 (22)	52 (15)	−35 (19)	3 (15)	−13 (23)
C(D5)	2620 (16)	868 (10)	5053 (13)	116 (20)	33 (13)	74 (16)	−14 (14)	22 (15)	−6 (14)
N(1)	1854 (12)	−329 (10)	3536 (11)	80 (14)	125 (18)	61 (14)	−12 (12)	4 (11)	1 (13)
C(1)	2251 (13)	−706 (13)	4067 (13)	70 (15)	100 (19)	81 (17)	−70 (18)	35 (14)	−53 (17)
S(1)	2878 (5)	−1287 (4)	4857 (5)	86 (5)	122 (6)	135 (7)	49 (5)	0 (5)	3 (5)
N(2)	2547 (13)	1823 (10)	2902 (12)	88 (16)	80 (15)	123 (17)	20 (13)	30 (13)	−24 (12)
C(2)	2957 (15)	2349 (12)	2893 (13)	99 (20)	91 (20)	62 (16)	7 (15)	23 (14)	23 (16)
S(2)	3603 (6)	3083 (4)	2991 (5)	189 (9)	101 (6)	148 (7)	−11 (5)	67 (6)	−60 (6)
N(3)	3013 (12)	336 (9)	2408 (10)	81 (15)	83 (14)	77 (14)	−10 (11)	15 (11)	2 (11)
C(3)	3518 (16)	−13 (12)	2122 (14)	78 (18)	103 (19)	88 (19)	−43 (17)	7 (15)	−4 (16)
S(3)	4238 (6)	−465 (5)	1718 (6)	140 (7)	224 (11)	174 (8)	−85 (7)	55 (6)	54 (7)
N(4)	537 (16)	1754 (10)	2463 (14)	183 (25)	80 (16)	172 (22)	46 (15)	119 (20)	25 (16)
C(4)	−106 (15)	2137 (11)	2147 (14)	80 (18)	55 (16)	113 (20)	−3 (15)	47 (16)	19 (13)
S(4)	−985 (5)	2644 (4)	1657 (5)	118 (6)	102 (6)	135 (7)	−2 (5)	36 (5)	43 (5)
N(5)	−52 (12)	271 (9)	2478 (11)	67 (13)	82 (13)	76 (12)	−10 (10)	24 (10)	−5 (11)
C(5)	−835 (13)	202 (11)	2365 (12)	40 (14)	94 (17)	70 (16)	7 (13)	17 (13)	−8 (13)
S(5)	−1971 (4)	112 (4)	2222 (4)	69 (5)	196 (8)	98 (5)	24 (6)	27 (4)	5 (5)
T	5678 (14)	1836 (11)	1554 (13)	U(iso) = 815 (18)					

[a] Value in parentheses is the estimated standard deviation in the last significant figure given in this and all following tables. [b] The thermal parameters are expressed in form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$, where the U_{ij} values are in Å^2.

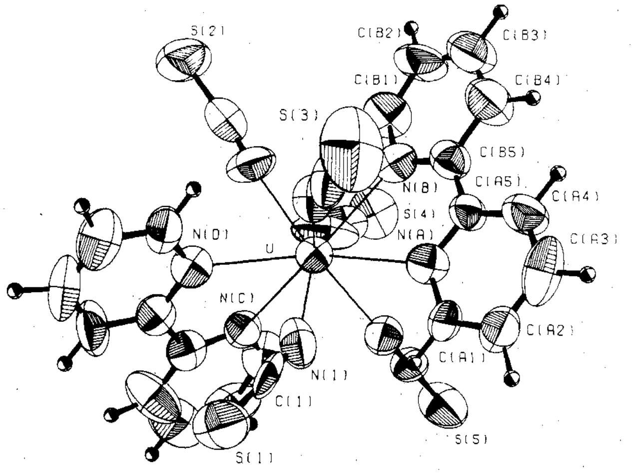

Figure 1. Perspective representation of the structure of the $[U(NCS)_5(bpy)_2]^-$ anion.

Table II. Fractional Coordinates ($\times 10^4$) for the Hydrogen Atoms[a]

atom	x	y	z
H(A1)	936	−1011	2331
H(A2)	834	−1977	1359
H(A3)	1084	−1694	−119
H(A4)	1315	−482	−535
H(B1)	1403	2268	1313
H(B2)	1586	2637	−66
H(B3)	1672	1765	−1153
H(B4)	1548	467	−821
H(C1)	−400	1284	3508
H(C2)	−996	1201	4857
H(C3)	114	1064	6300
H(C4)	1727	793	6363
H(D1)	3976	896	3710
H(D2)	5210	777	5033
H(D3)	4817	812	6390
H(D4)	3151	802	6451

[a] Hydrogen atoms placed at idealized positions 1 Å from their respective carbon atoms.

in Table III.. A set of coordination geometry parameters for both the normalized and unnormalized polyhedra are given in Table IV. Table V gives the average shape parameters for the normalized polyhedron as compared to those calculated by Robertson[10] as ideal. Figure 3 shows the ideal nine-coordinate polyhedra. Shape parameters for the seven-coordinate model are given in Table VI. Figure 4 shows the coordination polyhedron of the $[U(NCS)_5(bpy)_2]^-$ anion in which the bipyridine ligands have each been replaced by an atom B placed equidistant between the two coordinating nitrogen atoms and normalized. The relevant bond lengths and angles within the bipyridine ligands are given in Table VII. Relevant bond

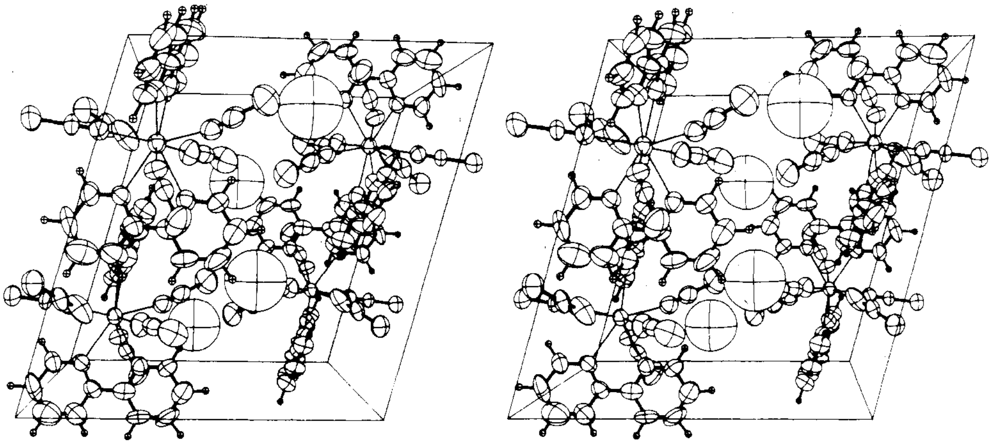

Figure 2. Stereo diagram of the unit cell and its contents viewed down the *b* axis. The large ellipsoid is the "T" atom.

Table III. Bond Distances and Spherical Angles for the $[U(NCS)_5(bpy)_2]^-$ Anion[a]

	r, Å	θ, deg	ϕ, deg
U-N(A)	2.65 (2)	0.000	0.000
U-N(B)	2.61 (2)	61.70	167.82
U-N(C)	2.63 (2)	136.44	306.81
U-N(D)	2.62 (2)	133.52	38.97
U-N(1)	2.35 (2)	75.93	0.000
U-N(2)	2.38 (2)	129.60	132.04
U-N(3)	2.40 (2)	66.64	83.32
U-N(4)	2.36 (2)	114.29	218.95
U-N(5)	2.47 (2)	67.87	277.63

[a] The spherical polar-coordinate system is defined relative to a Cartesian coordinate system oriented with the capping ligand N(A) on the *z* axis, with the *x* axis on the plane formed by the *z* axis and the U-N(1) vector. The angle θ is that between the *z* axis and the U-L vector, and ϕ is the angle from the *x* axis to the projection of the U-L vector on the *xy* plane.

lengths and angles for thiocyanato ligands are given in Table VIII.

Crystalline $[Et_4N]^+[U(NCS)_5(bpy)_2]^-$ consists of discrete anions and cations in which the uranium atoms display a coordination number 9. The task of assigning coordination polyhedra to nine-coordinate structures can be achieved in two basic ways. Muetterties and Guggenberger[9] have described a means of classifying real molecules by referencing them to ideal polyhedra via geometric pathways, which are characterized by the interfacial dihedral angles in the coordination group. Robertson[10] has also developed a similar method based on a different set of interfacial dihedral angles. In addition, Drew,[12] in his review of higher coordination compounds, used a method based on another different set of interfacial angles. In every case, however, the discussions were based on a unidentate ML_9 system rather than a $ML_5(AA)_2$ system and thus

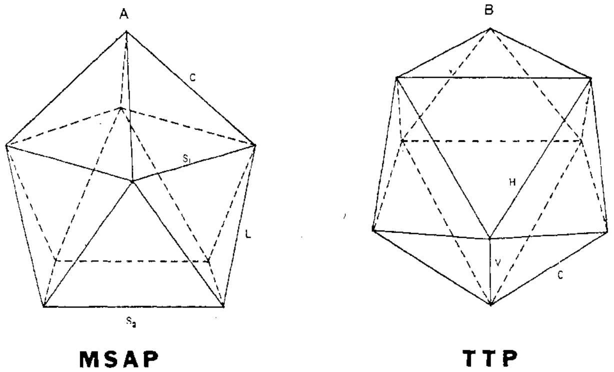

Figure 3. Ideal nine-coordination polyhedra.

Table IV. Shape Parameters for the $[U(NCS)_5(bpy)_2]^-$ Polyhedra

edge	type[a]	*d*, Å	d_{norm},[b] Å	interior angle,[c] deg	δ,[d] deg	δ_{norm},[b] deg
N(C)-N(1)	l	3.11 (2)	1.25	77.0 (5)	39.82	41.86
N(C)-N(5)	l	3.05 (2)	1.20	73.0 (5)	59.63	53.40
N(D)-N(1)	l	2.78 (2)	1.11	67.7 (5)	55.63	56.12
N(D)-N(3)	l	3.17 (2)	1.26	78.3 (5)	51.65	46.16
N(2)-N(B)	l	3.07 (3)	1.23	75.6 (6)	54.56	50.77
N(2)-N(3)	l	3.00 (3)	1.25	78.5 (6)	41.46	48.58
N(4)-N(B)	l	2.93 (3)	1.18	72.0 (6)	63.46	63.05
N(4)-N(5)	l	2.89 (3)	1.20	73.5 (7)	53.77	60.31
N(A)-N(B)	c	2.70 (2)	1.03	61.7 (5)	72.45	66.00
N(A)-N(1)	c	3.09 (2)	1.23	75.9 (5)	51.61	48.60
N(A)-N(3)	c	2.78 (2)	1.10	66.6 (5)	56.56	54.77
N(A)-N(5)	c	2.86 (2)	1.12	67.9 (5)	69.74	66.08
N(D)-N(4)	d	4.13 (3)	1.66	112.2 (14)	−19.17	−18.91
N(C)-N(2)	d	3.66 (2)	1.46	93.8 (17)	17.06	16.80
N(B)-N(3)	s_1	3.04 (2)	1.21	74.6 (5)	43.45	44.38
N(3)-N(1)	s_1	3.00 (2)	1.27	78.5 (6)	36.81	45.35
N(1)-N(5)	s_1	3.03 (2)	1.26	77.8 (6)	41.22	48.19
N(5)-N(B)	s_1	3.76 (2)	1.48	95.6 (15)	18.25	17.23
N(C)-N(D)	s_2	2.68 (2)	1.02	61.3 (5)	87.15	79.70
N(D)-N(2)	s_2	2.73 (2)	1.09	65.9 (6)	81.42	80.01
N(2)-N(4)	s_2	2.80 (3)	1.18	72.5 (6)	66.15	72.70
N(4)-N(C)	s_2	2.91 (3)	1.17	71.3 (6)	74.97	74.38

[a] Labeled according to Drew[12] for a capped square antiprism. The labeling scheme is indicated in Figure 1. [b] Calculated for the normalized polyhedron with all M-L distances equal to 1 Å. [c] The L-M-L angle. [d] The interfacial dihedral angle.

Table V. Average Shape Parameters for the $[U(NCS)_5(bpy)_2]^-$ Capped Square Antiprism

			ideal Coulombic[10]	
edge	d_{norm}, Å	δ_{norm}, deg	d, Å	δ, deg
4c	1.12 (8)	58.9 (87)	1.129	58.9
$8s_1$	1.21 (5)	52.5 (72)	1.183	52.7
$4s_1$	1.31 (12)	38.8 (145)	1.318	38.2
$4s_2$	1.12 (8)	76.7 (37)	1.119	69.1

Table VI. Shape Parameters of the Normalized Seven-Coordinate Polyhedra

edge	d, Å	δ, deg	edge	d, Å	δ, deg
B(1)-N(1)	1.60	24.5	B(2)-N(4)	1.44	53.5
B(1)-N(2)	1.58	33.4	B(2)-N(5)	1.54	37.0
B(1)-N(3)	1.11	86.7	N(1)-N(5)	1.26	79.3
B(1)-N(4)	1.46	55.1	N(5)-N(4)	1.20	80.7
B(1)-N(5)	1.29	73.9	N(4)-N(2)	1.18	81.1
B(2)-N(1)	1.14	85.9	N(2)-N(3)	1.25	81.2
B(2)-N(2)	1.27	75.2	N(3)-N(1)	1.27	81.2
B(2)-N(3)	1.62	21.3			

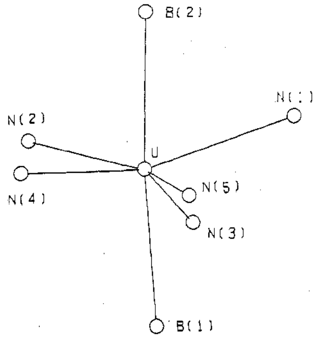

Figure 4. Projection of the seven-coordinate model onto the B(1), B(2), N(1), U plane.

are of limited usefulness in describing this type of complex.

The second method of assigning coordination polyhedra has been developed by Dollase[11] and used extensively by Drew in his review of higher coordination number compounds. In the Dollase method the normalized coordination polyhedron is compared directly to some polyhedron of ideal symmetry by least-squares minimization of the root-mean-square difference between the positions of the ideal polyhedron and those of the observed polyhedron. The root-mean-square difference (Δ) is given by

$$\Delta = \sum_{i=1}^{i=n} D_i^2/n$$

where n is the number of atoms in the coordination sphere and D_i is the distance between like points in the observed and ideal polyhedra.

The normalized observed coordination polyhedron was compared to the idealized polyhedra with symmetry C_{4v} for the MSAP and D_{3h} for the TTP. The values obtained for the two possibilities were $\Delta = 0.107$ for the MSAP and $\Delta = 0.236$ for the TTP. These results show conclusively that the coordination polyhedron in this compound is better described as a monocapped square antiprism in which the bipyridine ligands occupy positions on a c edge and an opposite s_2 edge.

The large distortion from ideal coordination geometry is primarily caused by the small bite of the bipyridine ligands. The bite of a bidentate ligand is defined as the average of the bond distance of the coordinating atoms to the metal divided by the distance between the two coordinating atoms. Thus the ligand bite of bipyridine in this compound is 0.98. For purposes of comparison to the ideal polyhedra, it is somewhat more informative to consider the distance between the two coordination atoms in the normalized coordination sphere. These are 1.03 Å for N(A)-N(B) and 1.02 Å for N(C)-N(D). Examination of the edge lengths of the ideal normalized polyhedra leads one to predict that the bipyridine ligands will occupy either c or s_2 edges of the MSAP or c edges of the TTP.

Table VII. Bond Lengths (Å) and Angles (Deg) of the Bipyridine Ligands

Distances

U-N(A)	2.65 (2)	U-N(B)	2.61 (2)
N(A)-C(A1)	1.35 (2)	N(B)-C(B1)	1.35 (2)
C(A1)-C(A2)	1.30 (2)	C(B1)-C(B2)	1.34 (3)
C(A2)-C(A3)	1.43 (3)	C(B2)-C(B3)	1.36 (3)
C(A3)-C(A4)	1.34 (3)	C(B3)-C(B4)	1.42 (3)
C(A4)-C(A5)	1.35 (2)	C(B4)-C(B5)	1.45 (3)
C(A5)-N(A)	1.33 (2)	C(B5)-N(B)	1.38 (2)
C(A5)-C(B5)	1.39 (2)		
U-N(C)	2.63 (2)	U-N(D)	2.62 (2)
N(C)-C(C1)	1.30 (2)	N(D)-C(D1)	1.30 (2)
C(C1)-C(C2)	1.45 (3)	C(D1)-C(D2)	1.37 (3)
C(C2)-C(C3)	1.37 (3)	C(D2)-C(D3)	1.32 (3)
C(C3)-C(C4)	1.33 (3)	C(D3)-C(D4)	1.34 (3)
C(C4)-C(C5)	1.38 (3)	C(D4)-C(D5)	1.39 (2)
C(C5)-N(C)	1.36 (2)	C(D5)-N(D)	1.30 (2)
C(C5)-C(D5)	1.47 (2)		

Angles

N(A)-U-N(B)	61.7 (5)	N(C)-U-N(D)	61.3 (5)
C(A1)-N(A)-C(A5)	120 (3)	C(C1)-N(C)-C(C5)	116 (3)
N(A)-C(A1)-C(A2)	124 (3)	N(C)-C(C1)-C(C2)	122 (4)
C(A1)-C(A2)-C(A3)	115 (4)	C(C1)-C(C2)-C(C3)	119 (5)
C(A2)-C(A3)-C(A4)	121 (4)	C(C2)-C(C3)-C(C4)	119 (5)
C(A3)-C(A4)-C(A5)	120 (4)	C(C3)-C(C4)-C(C5)	119 (4)
C(A4)-C(A5)-N(A)	120 (3)	C(C4)-C(C5)-N(C)	124 (3)
C(A4)-C(A5)-C(B5)	123 (3)	C(C4)-C(C5)-C(D5)	119 (3)
C(A5)-C(B5)-C(B4)	121 (3)	C(C5)-C(D5)-C(D4)	123 (3)
C(B1)-N(B)-C(B5)	117 (3)	C(D1)-N(D)-C(D5)	117 (3)
N(B)-C(B1)-C(B2)	126 (4)	N(D)-C(D1)-C(D2)	124 (3)
C(B1)-C(B2)-C(B3)	120 (4)	C(D1)-C(D2)-C(D3)	118 (4)
C(B2)-C(B3)-C(B4)	118 (4)	C(D2)-C(D3)-C(D4)	121 (4)
C(B3)-C(B4)-C(B5)	120 (4)	C(D3)-C(D4)-C(D5)	118 (4)
C(B4)-C(B5)-N(B)	119 (4)	C(D4)-C(D5)-N(D)	121 (3)

Table VIII. Bond Distances (Å) and Angles (Deg) of the Thiocyanato Ligands

Distances

U-N(1)	2.35 (2)	N(1)-C(1)	1.13 (3)
U-N(2)	2.38 (2)	N(2)-C(2)	1.15 (2)
U-N(3)	2.40 (2)	N(3)-C(3)	1.15 (2)
U-N(4)	2.36 (2)	N(4)-C(4)	1.17 (2)
U-N(5)	2.47 (2)	N(5)-C(5)	1.10 (2)
C(1)-S(1)	1.72 (2)	C(4)-S(4)	1.61 (2)
C(2)-S(2)	1.64 (2)	C(5)-S(5)	1.60 (2)
C(3)-S(3)	1.59 (2)		

Angles

U-N(1)-C(1)	155 (2)	N(1)-C(1)-S(1)	178 (2)
U-N(2)-C(2)	174 (2)	N(2)-C(2)-S(2)	174 (2)
U-N(3)-C(3)	161 (2)	N(3)-C(3)-S(3)	178 (2)
U-N(4)-C(4)	163 (2)	N(4)-C(4)-S(4)	177 (2)
U-N(5)-C(5)	165 (2)	N(5)-C(5)-S(5)	179 (2)

Additional distortion in the coordination polyhedron is caused by a number of close contacts between nitrogen atoms of thiocyanato ligands and hydrogen atoms in 6,6′ positions on the bipyridine ligands which are within the sum of van der Waals radii for N and H which is 2.7 Å.[21] These contacts are between N(1) and H(A1), N(3) and H(D1), N(4) and H(C1), N(4) and H(B1), and N(5) and H(C1) and are equal to 2.38, 2.39, 2.54, 2.62, and 2.63 Å respectively. The distortion caused by the small ligand bites and the crowding within the complex makes it difficult to assign the polyhedron as either MSAP or TTP except by the method of Dollase and makes it impossible to assign the coordination geometry to

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(21) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p 260.

some position along the geometric pathway relating the two ideal nine-coordinate polyhedra. It is interesting to note that in spite of the large distortion present in this complex the average shape parameters as shown in Table V compare quite closely to Robertson's ideal values for the charged monocapped square antiprism.

We believe that one of the major purposes of assigning coordination polyhedra to real complexes is to aid in visualization of the complex. For this reason a model based on the seven-coordinate pentagonal bipyramid was examined. The bipyridine ligands were considered to occupy single coordination sites by placing atoms B(1) and B(2) equidistant between N(A) and N(B) and between N(C) and N(D), respectively, and normalizing them. The two positions can be considered to occupy the two axial positions of a pentagonal bipyramid with the five thiocyanato ligands forming the pentagonal girdle.

Figure 4 shows a projection of the coordination group onto the best plane through atoms B(1), N(1), U, and B(2). Best planes were calculated for the bipyridine ligands, and the dihedral angle between them was calculated to be 90.1°. Deviations of carbon atoms from the calculated best planes do not exceed 0.10 Å. The B(1)-U-B(2) angle was calculated to be 174.7°. The equatorial plane N(2), N(3), N(4), and N(5) is perpendicular (90.7°) to the quasi mirror plane. In this figure the bipyridine ligand represented by B(1) is in the plane of the paper while the bipyridine ligand represented by B(2) is approximately perpendicular to the plane of the paper. The close contact of 2.37 Å between N(1) and H(A1) causes atom N(1) to be pushed up away from the equatorial plane. Close contacts between N(3) and H(D1) and between N(5) and H(C1) of 2.39 and 2.62 Å cause these two atoms to be displaced downward away form the equatorial plane. Shape parameters for the seven-coordinate model are found in Table VI.

Uranium-nitrogen bond lengths are between 2.61 and 2.65 Å for the two bipyridine ligands. Uranium-nitrogen bond distances for the five thiocyanato ligands vary between 2.35 and 2.47 Å, in reasonable agreement with the uranium-nitrogen bond distance of 2.38 Å in $[(Et_4N)_4]^{4+}[U(NCS)_8]^{4-}$.[22] Nitrogen-carbon bond distances of 1.10-1.17 Å agree with distances reported for other structures containing the thiocyanato group as do the carbon-sulfur bond distances of 1.59-1.72 Å. N-C-S bond angles are all effectively 180° as expected for the predominantly sp-hybridized interligand bonding. U-N-C bond angles of 155, 161, 163, 165, and 174° differ significantly from the theoretical value of 180°. Deviations from linearity of M-N-C bond angles in thiocyanato ligands have been reported previously[23] and are attributed to crystal-packing effects. Close contacts between the sulfur atoms of the thiocyanato ligands and hydrogen atoms of the tetraethylammonium cation are presumably the cause of the distortion; in this case, however, incomplete resolution of the tetraethylammonium ion made calculation of these contacts impossible.

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Registry No. $[Et_4N]^+[U(NCS)_5(bpy)_2]^-$, 74511-91-4; $(Et_4N)_4U(NCS)_8$, 33724-34-4.

Supplementary Material Available: Structure factor tables (32 pages). Ordering information is given on any current masthead page.

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Relation between the Structure and Spectra of Pseudotetrahedral CuN_4 Complexes and the Crystal Structure of $[CuL_2](ClO_4)_2$, L = 2-Pyridyl-2-pyrimidylamine

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The crystal structure of the title complex has been determined. The copper environment is pseudotetrahedral, with a dihedral angle, ϕ, of 53.8° between the two CuN_2 ligand planes. The two ligands are identical as required by crystallographic symmetry. The two perchlorate groups are ionic, 3.369 (1) Å away from the copper atom on opposite sides. This result suggests the hypothesis of a correlation between the spectra and structures of pseudotetrahedral CuN_4 species. The electronic spectrum of $[Cu(MPA)_2]$, which has $\phi = 57.4°$, is very similar to that of $[Cu(PTA)_2]$, suggesting similar values of ϕ for the two complexes and contradicting an earlier postulate of a less tetrahedral structure for $[Cu(PTA)_2]$ (HMPA = 3,3′-dimethyl-2,2′-dipyridylamine, HPTA = 2-pyridyl-2-thiazolylamine). Crystal data for $[Cu(HPPA)_2](ClO_4)_2$: space group $C2/c$, $Z = 4$, $a = 9.356$ (8) Å, $b = 12.752$ (2) Å, $c = 19.353$ (4) Å, $\beta = 101.56$ (3)°, $V = 2262$ Å^3, $R = 4.6\%$ for 1893 reflections.

Introduction

The CuN_4 chromophore usually has a square-planar structure in four-coordinate copper(II) complexes. The series of complexes with general formulas $Cu(HL)_2(ClO_4)_2$ and $Cu(L)_2$,[2] however, contain CuN_4 chlorophores that have pseudotetrahedral structures.[3] These geometries have been assigned by crystallographic studies[4,5] and by analysis of the electronic spectra of members of these series.[3]

The differences in the band positions of the d-d transitions in the electronic spectra suggest differences in the dihedral

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[2] In this paper HL is the generic name for a bidentate ligand and L^- is the deprotonated form. Specific names: 2,2′-dipyridylamine, HDPA; 2-pyridyl-2-pyrimidylamine, HPPA; 2-pyridyl-2-thiazolylamine, HPTA; 3,3′-dimethyl-2,2′-dipyridylamine, HMPA.

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