38 kJ for the two ethylene glycol media. These values can be associated with given correlation lengths if we invoke a given functional form for the medium-dipole correlation functions. If the correlation between the dipoles can be represented by an exponentially decaying function of decay length λ, this provides well-defined tractable expressions for $F(x)$ and $\tilde{F}(x)$,[16] from which E_s can be calculated for given values of λ. Following this procedure, a value of $\lambda \approx 1.5r \approx 4$ Å is necessary to reproduce the "experimental" change in E_s.

Introduction of a temperature-dependent correlation length which describes the increasing organization of the medium with decreasing temperature can thus account for the observed effects for reasonable values of the appropriate correlation length. Our approach also shows that when rate constants are measured over large temperature intervals, all the effects considered above must be invoked, but a proper choice of system (e.g., electrically neutral reactants) may well provide reasonable estimates of their individual contributions.

Registry No. $[Co(NH_3)_5H_2O]^{3+}$, 14403-82-8; $[Ru(NH_3)_6]^{2+}$, 19052-44-9; $[Co(NH_3)_5H_2O]^{2+}$, 22045-50-7; $[Ru(NH_3)_6]^{3+}$, 18943-33-4.

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X-ray Crystal and Molecular Structure of Tris(*N*,*N*-diethyldithiocarbamato)-bis[μ-(*N*,*N*-diethyltrithiocarbamato)]-diosmium(III) Tetraphenylborate. The First Example of a Sulfur-Rich Dithiocarbamate

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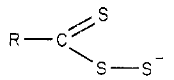
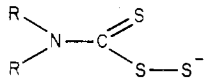
Examples of metal complexes which contain sulfur-rich dithiocarboxylates or perthiocarboxylates (I, R = aryl or alkyl)



I

as ligands are well-known.[1-4] These complexes are generally formed by the oxidative addition of elemental sulfur or anionic polysulfides to transition-metal dithio acid complexes. Several of these complexes have been characterized by single-crystal X-ray analyses.[1,2] Analogous sulfur-rich N,N-disubstituted dithiocarbamato (II), $^-S_3CNR_2$, complexes have not been



II

observed,[5] although there has been considerable interest in such species because they are thought to be key intermediates in rubber vulcanization accelerated by zinc dithiocarbamates.[6,7] It has been proposed that perthiocarbamates are the source of the sulfidic cross-links in the vulcanized-rubber matrix.[6,7] During our studies on the structural and redox chemistry of the dithiocarbamato complexes of osmium,[8,9] we isolated crystals of a novel sulfur-rich (*N*,*N*-diethyldithiocarbamato)diosmium complex, $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]BPh_4$. A single-crystal X-ray analysis provides unambiguous evidence for the existence of the trithiocarbamate ligand.

Experimental Section

Crystals of $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]BPh_4$ were isolated as a byproduct in the synthesis of $Os(S_2CNEt_2)_3$ and $[Os_2(S_2CNEt_2)_5]^+$.[8] The actual procedure used varied slightly from the one reported in ref 8. $(NH_4)_2[OsCl_6]$ (2.3 mmol) was reacted with NaS_2CNEt_2 (9.0 mmol) in refluxing $MeOH/H_2O$ (200 mL, 50:50 v/v) under a N_2 atmosphere for 20 h. The brown precipitate was extracted with CH_2Cl_2 and column chromatographed (alumina, Alcoa F-20). Elution with CH_2Cl_2 removed $Os(S_2CNEt_2)_3$ (orange band) in ca. 50% yield based on osmium. The column was then eluted with acetone until the collected fractions were colorless. Finally, elution with methanol removed a brown band. The brown methanol solution was reduced in volume, and upon addition of $NaBPh_4$ a brown precipitate formed. This solid was extracted with CH_2Cl_2 and column chromatographed on alumina. Elution with CH_2Cl_2 removed a brown band which presumably contains a mixture of $[Os_2(S_2CNEt_2)_5]BPh_4$ and $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]BPh_4$. Crystals of the latter were obtained by the vapor-diffusion technique with acetone and ethyl ether. The final yield of this compound was less than 5% on the basis of osmium. None of the crystals were of high quality, and a small elongated rectangular needle (0.10 × 0.05 × 0.02 mm) was used for data collection. The cell constants, $a = 13.595$ (4) Å, $b = 18.492$ (7) Å, $c = 13.320$ (20) Å, $\alpha = 98.68$ (6)°, $\beta = 112.55$ (7)°, and $\gamma = 94.02$ (3)°, were determined by least-squares refinement of the angular settings of 25 Mo Kα ($\lambda = 0.71069$ Å) reflections centered on a CAD 4 diffractometer using the Enraf-Nonius automatic peak-centering

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Table I

Positional and Thermal Parameters and Their Esd's

atom	x	y	z	B, Å^2
Os1	0.2467 (1)	0.0604 (1)	0.0663 (1)	2.2^a
Os2	0.2593 (2)	0.0619 (1)	−0.1377 (1)	2.8^a
SA1	0.1601 (10)	−0.0581 (7)	−0.2368 (10)	4.3 (3)
SA2	0.3527 (9)	0.0046 (7)	−0.2410 (9)	3.6 (3)
SB1	0.3663 (9)	0.1806 (7)	−0.0990 (9)	3.9 (3)
SB2	0.1797 (9)	0.1228 (7)	−0.2931 (9)	3.8 (3)
SC1	0.3499 (9)	0.0372 (6)	0.2507 (9)	3.1 (3)
SC2	0.1404 (9)	0.0796 (7)	0.1775 (9)	3.5 (3)
SD1	0.1264 (10)	0.0963 (7)	−0.0857 (10)	4.7 (3)
SD2	0.3213 (9)	0.1875 (7)	0.1348 (9)	3.9 (3)
SD3	0.1248 (13)	0.2082 (9)	−0.0528 (13)	7.4 (4)
SE1	0.3821 (8)	0.0271 (6)	0.0142 (8)	2.9 (2)
SE2	0.1639 (9)	−0.0634 (6)	0.0126 (9)	3.2 (3)
SE3	0.3808 (9)	−0.0844 (7)	0.0089 (9)	3.8 (3)
NA	0.248 (3)	−0.128 (2)	−0.366 (3)	5.2 (10)
NB	0.303 (3)	0.254 (2)	−0.268 (3)	5.9 (11)
NC	0.240 (3)	0.057 (2)	0.385 (3)	3.6 (8)
ND	0.263 (3)	0.314 (2)	0.094 (3)	6.2 (11)
NE	0.234 (4)	−0.196 (3)	−0.014 (4)	10.1 (16)
CA	0.258 (3)	−0.068 (2)	−0.291 (3)	2.9 (10)
CA1	0.162 (4)	−0.208 (3)	−0.386 (4)	6.4 (14)
CA2	0.337 (3)	−0.140 (2)	−0.408 (3)	4.1 (11)
CA3	0.093 (7)	−0.183 (5)	−0.442 (7)	15.7 (33)
CA4	0.411 (4)	−0.187 (3)	−0.329 (4)	5.1 (13)
CB	0.272 (4)	0.197 (3)	−0.230 (4)	4.8 (12)
CB1	0.403 (4)	0.307 (3)	−0.212 (4)	6.2 (14)
CB2	0.225 (4)	0.266 (3)	−0.380 (4)	7.5 (16)
CB3	0.382 (3)	0.366 (2)	−0.132 (3)	4.3 (12)
CB4	0.156 (6)	0.317 (4)	−0.370 (6)	13.5 (27)
CC	0.255 (3)	0.051 (2)	0.287 (3)	3.9 (11)
CC1	0.333 (4)	0.029 (3)	0.470 (4)	6.3 (14)
CC2	0.151 (4)	0.067 (3)	0.408 (4)	5.6 (13)
CC3	0.418 (4)	0.100 (3)	0.550 (4)	5.2 (13)
CC4	0.089 (4)	−0.001 (3)	0.415 (4)	5.1 (13)
CD	0.237 (4)	0.241 (3)	0.058 (4)	4.8 (12)
CD1	0.220 (5)	0.377 (4)	0.021 (6)	11.3 (23)
CD2	0.364 (5)	0.348 (4)	0.204 (5)	9.3 (20)
CD3	0.114 (5)	0.376 (3)	0.059 (5)	8.8 (19)
CD4	0.463 (5)	0.369 (4)	0.177 (6)	10.9 (24)
CE	0.253 (3)	−0.125 (2)	−0.003 (3)	2.6 (9)
CE1	0.121 (3)	−0.226 (2)	−0.026 (3)	3.6 (11)
CE2	0.321 (3)	−0.248 (2)	0.001 (3)	4.1 (11)
CE3	0.042 (3)	−0.24 (3)	−0.144 (4)	4.5 (12)
CE4	0.311 (4)	−0.260 (3)	−0.115 (4)	6.3 (15)
B	0.305 (5)	−0.371 (3)	−0.693 (5)	5.5 (16)
C1	0.263 (2)	−0.272 (2)	−0.708 (2)	4.4 (7)
C2	0.326 (3)	−0.232 (3)	−0.721 (4)	4.4 (12)
C3	0.300 (4)	−0.158 (3)	−0.738 (4)	5.2 (13)
C4	0.198 (3)	−0.152 (2)	−0.737 (3)	3.7 (11)
C5	0.131 (3)	−0.199 (2)	−0.712 (3)	4.1 (11)
C6	0.170 (4)	−0.274 (3)	−0.698 (4)	4.8 (12)
C7	0.273 (4)	−0.408 (3)	−0.833 (4)	5.1 (13)
C8	0.169 (4)	0.592 (3)	0.101 (4)	7.4 (16)
C9	0.144 (4)	−0.438 (3)	−1.028 (4)	5.2 (13)
C10	0.227 (4)	−0.457 (3)	−1.052 (5)	7.3 (16)
C11	0.328 (4)	−0.450 (3)	−0.982 (4)	7.2 (16)
C12	0.355 (3)	−0.430 (3)	−0.865 (4)	4.5 (12)
C13	0.242 (4)	−0.416 (3)	−0.635 (4)	6.2 (14)
C14	0.159 (4)	0.521 (3)	0.308 (5)	7.9 (17)
C15	0.106 (4)	0.482 (3)	0.374 (5)	7.9 (17)
C16	0.138 (5)	−0.481 (4)	−0.524 (5)	10.6 (22)
C17	0.220 (5)	−0.423 (4)	−0.462 (5)	10.1 (21)
C18	0.258 (5)	−0.387 (4)	−0.526 (5)	9.8 (20)
C19	0.431 (3)	−0.367 (3)	−0.614 (4)	4.4 (12)
C20	0.491 (4)	0.699 (3)	0.460 (4)	5.5 (13)
C21	0.396 (4)	0.303 (3)	0.470 (4)	4.9 (12)
C22	0.338 (4)	0.371 (3)	0.469 (5)	7.5 (16)
C23	0.580 (4)	0.571 (3)	0.459 (4)	7.3 (16)
C24	0.474 (4)	0.567 (3)	0.387 (4)	6.4 (15)

Anistropic Thermal Parameters ($\times 10^4$)^b

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os1	48 (1)	18.2 (5)	23 (1)	15 (1)	10 (2)	15 (1)
Os2	52 (1)	29.9 (7)	24 (1)	8 (2)	18 (2)	13 (1)

[a] Refined anisotropically; equivalent isotropic B is listed. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \ldots + \beta_{12}hk + \ldots)]$.

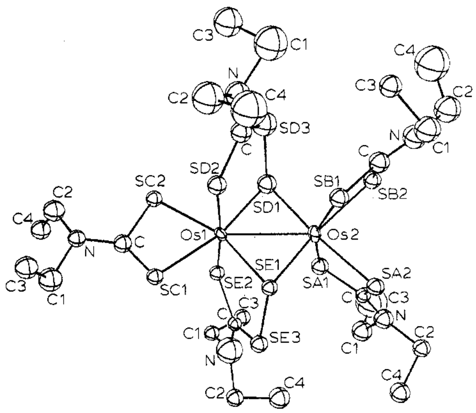


Figure 1. ORTEP drawing of the cation $Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2^+$.

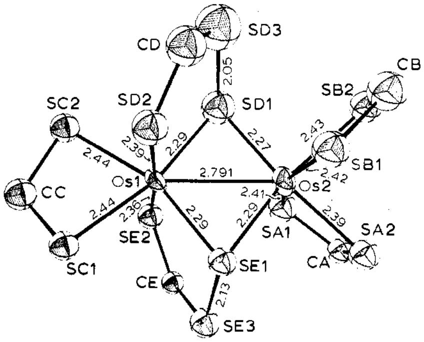


Figure 2. ORTEP drawing of the $Os_2S_{12}C_5$ coordination core with selected distances in angstroms.

program.[10a] Successful solution and refinement were achieved by using the centric space group $P\bar{1}$ ($V = 3027$ Å^3, $Z = 2$). A total of 7816 unique reflections were measured in the scan range $2\theta = 0$–$50°$ on an Enraf-Nonius CAD 4 automatic diffractometer using graphite-monochromatized Mo Kα radiation and employing a variable-rate ω–2θ scan technique. After correction for Lorentz, polarization, background, and absorption ($\mu = 48.9$ cm^{-1}) effects,[10a] only 2534 (32%) were judged observed ($F_o^2 \geq 2.5\sigma(F_o^2)$) and were used in all subsequent calculations.[10b] Conventional heavy-atom techniques were used to solve the structure, and refinement, with the osmium atoms thermally anistropic and the remaining nonhydrogen atoms isotropic by full-matrix least-squares methods (287 variables), converged R and R_w to their final values of 0.078 and 0.086, respectively.[11] The error in an observation of unit weight was 1.76 by using a value of 0.06 for p in the $\sigma(I)$ equation.[10,11] In the final difference Fourier, the highest peak was 1.9 e Å^{-3} in the vicinity of an osmium atom. The highest peak not near an atom was 0.9 e Å^{-3}.

The final atomic coordinates with their estimated standard deviations and the final thermal parameters are given in Table I. A table of observed and calculated structure factors is available (supplementary material). Figure 1 presents an ORTEP perspective of the molecular structure of the cation and shows the labeling scheme. The carbon atoms of the four phenyl rings in the BPh_4 anion are labeled C1–C6, C7–C12, C13–C18, and C19–C24, respectively.

Results and Discussion

The structure consists of well-separated $Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2$ cations and BPh_4 anions. The shortest intermolecular contact is 3.38 Å for the C10 (of BPh_4)–CD1 distance. The distances and angles within the BPh_4 anion are normal, and all phenyl rings are planar within experimental error. The structure of the cation is similar to that of α-$[Ru_2(S_2CN\text{-}i\text{-}Pr_2)_5]^+$[12] except that each of the two bridging chelate rings of the osmium complex has been expanded by the addition of an extra sulfur atom and the overall stereochemistry is somewhat different (vide infra). Important distances and angles within the diosmium coordination core are shown in Figure 2 and Table II. These data clearly establish the presence of the trithiocarbamate ligand, although in a rather

Table II. Selected Intramolecular Distances and Angles within the Coordination Core

Distances, A

Os1-Os2	2.791 (2)	Os2-SA2	2.39 (1)	SD2-SD1	3.23 (2)
Os1-SC1	2.44 (1)	Os2-SB1	2.42 (1)	SD2-SD3	2.97 (2)
Os1-SC2	2.44 (1)	Os2-SB2	2.43 (1)	SE2-SE1	3.29 (1)
Os1-SD1	2.29 (1)	Os2-SD1	2.27 (1)	SE2-SE3	3.04 (1)
Os1-SD2	2.39 (1)	Os2-SE1	2.29 (1)	SA1-SA2	2.81 (1)
Os1-SE1	2.29 (1)	SD1-SD3	2.05 (2)	SB1-SB2	2.83 (1)
Os1-SE2	2.36 (1)	SE1-SE3	2.13 (1)	SC1-SC2	2.85 (1)
Os2-SA1	2.41 (1)			SD1-SE1	3.62 (1)

Angles, Deg

SC1-Os1-SC2	71.3 (3)	Os1-SD1-SD3	110.0 (7)	Os1-SE1-SE3	106.9 (5)
SD1-Os1-SD2	87.3 (4)	Os2-SD1-SD3	115.1 (7)	Os2-SE1-SE3	116.3 (5)
SE1-Os1-SE2	90.2 (4)	SD2-Os1-SC2	87.2 (4)	SB1-Os2-SD1	100.3 (4)
SA1-Os2-SA2	71.7 (4)	SD2-Os1-SC1	88.1 (3)	SB1-Os2-SE1	92.2 (4)
SB1-Os2-SB2	71.6 (4)	SD2-Os1-SE1	95.4 (4)	SB1-Os2-SA2	92.2 (4)
SD1-Os1-SE1	104.3 (4)	SC2-Os1-SD1	95.4 (4)	SE1-Os2-SA2	87.0 (4)
SD1-Os2-SE1	105.1 (4)	SC1-Os1-SE1	89.2 (3)	SD1-Os2-SB2	86.2 (4)
Os1-SD1-Os2	75.6 (4)	SE2-Os1-SC2	86.6 (3)	SA1-Os2-SE1	98.9 (4)
Os1-SE1-Os2	75.0 (3)	SE2-Os1-SD1	94.2 (4)	SA1-Os2-SD1	93.2 (4)
		SE2-Os1-SC1	89.2 (3)	SA1-Os2-SB2	94.5 (4)

Table III. Intramolecular Distances and Angles within the Ligands

Distances, A

	ligand						ligand				
	A	B	C	D	E		A	B	C	D	E
S1-S3				2.05 (2)	2.13 (1)	N-C1	1.72 (5)	1.48 (5)	1.52 (5)	1.61 (6)	1.53 (5)
S3-C				1.66 (4)	1.76 (3)	N-C2	1.53 (4)	1.53 (5)	1.38 (5)	1.58 (6)	1.56 (5)
S1-C	1.74 (3)	1.82 (4)	1.58 (4)			C1-C3	1.14 (8)	1.53 (5)	1.62 (6)	1.70 (7)	1.50 (5)
S2-C	1.66 (3)	1.67 (4)	1.85 (4)	1.71 (4)	1.76 (3)	C2-C4	1.57 (5)	1.40 (7)	1.50 (5)	1.56 (7)	1.48 (5)
C-N	1.34 (4)	1.33 (5)	1.37 (4)	1.34 (5)	1.30 (5)						

Angles, Deg

Os2-SA1-CA	87 (1)	Os1-SC1-CC	91 (1)	SD1-SD3-CD	105 (2)	SC1-CC-SC2	112 (2)
Os2-SA2-CA	90 (1)	Os1-SC2-CC	85 (1)	SE1-SE3-CE	107 (1)	SD2-CD-SD3	124 (3)
Os2-SB1-CB	88 (1)	Os1-SD2-CD	110 (1)	SA1-CA-SA2	111 (2)	SE2-CE-SE3	119 (2)
Os2-SB2-CB	91 (1)	Os1-SE2-CE	112 (1)	SB1-CB-SB2	109 (2)		

unusual coordinating mode. The average S–S distance in the five-membered chelate ring of 2.09 (1) Å compares favorably with those of sulfur-rich dithiocarboxylates which range from 2.01 to 2.09 Å[1,2] and with the average value of 2.06 Å reported[13] for a number of compounds containing S–S bonds. The distances and angles within the five-membered sulfur-rich chelate rings are similar to those found for complexes of trithiocarboxylates.[1,2] The S1, S2, S3, and C atoms of sulfur-rich ligands D and E form essentially planar groupings with Os1 displaced 0.48 and 0.58 Å, respectively, from the weighted least-squares planes (see Table IV). The S_2CN atoms of the normal dithiocarbamate ligands are approximately planar, and the distances and angles within these ligands compare well with those in other S_2CNR_2 metal complexes (Tables III and IV). The average Os–S distance for the dithiocarbamate ligands is 2.42 (1) Å compared with 2.40 (2) Å observed in $Os_2N(S_2CNMe_2)_5$, which is the only other Os dithiocarbamate complex which has been structured by single-crystal X-ray analysis.[9] The average S–Os–S four-membered chelate "bite" angle for the dithiocarbamate ligands is 71.5 (4)° compared with 73 (1)° for $Os_2N(S_2CNMe_2)_5$.[9] In the five-membered sulfur-rich chelate rings the Os–S distances are shortened to 2.37 (1) Å (nonbridging) and 2.29 (1) Å (bridging) while the chelate bite angles are enlarged to 88.8 (4)°. The shortening of the bridging M–S bonds has been observed in other bimetallic dithiocarbamate complexes of ruthenium.[12,14]

The Os–Os distance of 2.791 (2) Å is comparable to the Ru–Ru distance of 2.789 (4) Å found in α-$[Ru_2(S_2CN\text{-}i\text{-}Pr_2)_5]^+$ and indicates metal–metal bonding.[12,14] The overall sterochemistry of the cation is best appreciated by viewing the ORTEP stereoview (Figure 3). It is apparent that the geometry about each Os atom is that of a distorted tris-chelated octa-

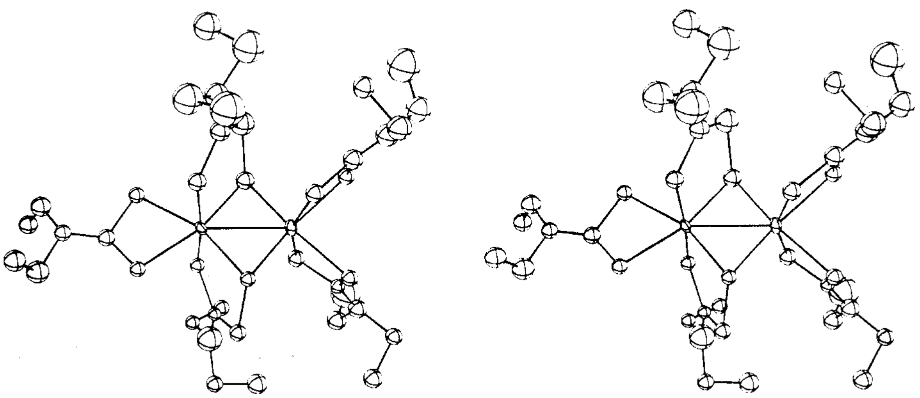
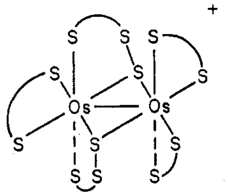


Figure 3. ORTEP stereoview of the cation.

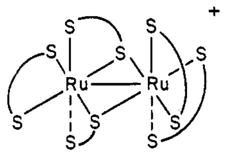
Table IV. Weighted Least-Squares Planes

plane no.	atoms forming plane	 other	dist from plane, Å (esd)
1	SD1		0.003 (14)
	SD2		−0.004 (13)
	SD3		−0.011 (18)
	CD		0.104 (50)
		Os1	−0.484 (2)
2	SE1		0.004 (10)
	SE2		−0.006 (11)
	SE3		−0.011 (11)
	CE		0.127 (35)
		Os1	−0.582 (2)
3	SA1		0.000 (12)
	SA2		0.000 (12)
	CA		−0.015 (39)
	NA		0.006 (37)
		Os2	0.097 (2)
4	SB1		0.002 (13)
	SB2		0.003 (13)
	CB		−0.125 (51)
	NB		0.041 (44)
		Os2	0.152 (2)
5	SC1		−0.001 (12)
	SC2		−0.001 (12)
	CC		0.060 (45)
	NC		−0.015 (35)
		Os1	0.014 (2)
6	Os1		0.000 (2)
	Os2		0.000 (2)
	SD1		−0.016 (14)
	SE1		−0.011 (17)
		SD3	−1.816 (17)
		SE3	1.848 (12)

hedron, each possessing the same chirality (Δ,Δ as shown). It is interesting that in α-$[Ru_2(S_2CN\text{-}i\text{-}Pr_2)_5]^+$ the two distorted tris-chelated octahedrons have opposite chiralities[12] as shown in the line drawings. The two osmium atoms are



$Os_2(dtc)_3(Sdtc)_2{}^+$
(Δ,Δ)



α-$[Ru_2(dtc)_5]^+$
(Δ,Λ)

symmetrically bridged by SD1 and SE1, and the Os1, Os2, SD1, and SE1 atoms form a plane within experimental error (Table IV). The dihedral angles between plane 6 (Os1, Os2, SD1, SE1) and planes 1 (SD1, SD2, SD3, CD) and 2 (SE1, SE2, SE3, CE) are 73.8 and 72.1°, respectively (Table IV).

Since only a small quantity of $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]BPh_4$ has thus far been isolated, other characterization data and chemical properities have not yet been determined. However, the X-ray analysis unambiguously establishes the existence of the trithiocarbamate ligand. Relevant experiments in progress are designed to improve the yield of this sulfur-rich compound via alternate synthetic routes and to elucidate the chemical properties of the trithiocarbamate ligand.

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Registry No. $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]BPh_4$, 71341-62-3.

Supplementary Material Available: Observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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(10) (a) The intensity data were precessed as described in: "CAD4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity I is given as $I = [K/(\mathrm{NPI})](C - 2B)$, where $K = 20.1166$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = [K/(\mathrm{NPI})]^2[C + 4B + (pI)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz–polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors, (F_o), by $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$. (b) All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP programs. This crystallographic computing package is described in the following reference: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., and Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.
(11) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\alpha^2(F_o)$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|))^2/\sum w|F_o|^2]^{1/2}$. The error in an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NW are the number of observations and variables, respectively.
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