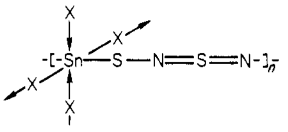

G

The nitrogen or sulfur atoms of the S_2N_2 moiety could also participate in bridging to tin as the nitrogen atoms in the dimeric 5,5-dimethyl-1,3λ^4,2,4,5-dithiadiazastannole do.[26] Methoxy bridging occurs in trimethyltin(IV) methoxide,[27] and we have recently proposed bridging by dimethylamino groups in tin(IV) amines on the basis of variable-temperature Mössbauer studies.[28] There is no precedent, however, for the latter structure (G), and the former structure (F) would appear to be more likely in the dihalo derivatives. The bridged or cross-linked structures F and G would account for the insoluble and infusible nature of these products, however. Infrared data is of limited utility, other than to confirm the presence of the OCH_3 and $N(CH_3)_2$ groupings from the ν(C–H) and δ(C–H) absorptions.

Acknowledgment. Our work is supported by the Office of Naval Research and by the National Science Foundation under Grant CHE-78-26584.

Registry No. $SnCl_4 \cdot 2S_4N_4$, 24046-65-9; $SnBr_4 \cdot 2S_4N_4$, 67735-19-7; $SnCl_2 \cdot S_2N_2$, 81245-11-6; $SnBr_2 \cdot S_2N_2$, 81245-12-7; $Sn(OCH_3)_2 \cdot S_2N_2$, 81245-15-0; $(SN)_2Sn[N(CH_3)_2]_2$, 81245-17-2; S_4N_4, 28950-34-7; $SnCl_4$, 7646-78-8; $SnBr_4$, 7789-67-5; $SnCl_2$, 7772-99-8; $SnBr_2$, 10031-24-0; $Sn(OCH_3)_2$, 37182-97-1; $Sn[N(CH_3)_2]_2$, 81245-13-8.

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Crystal and Molecular Structure of $[Nd(tren)_2(CH_3CN)](ClO_4)_3$

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Received August 3, 1981

Lanthanide coordination chemistry is dominated by oxygen-donor ligands, especially by chelate ligands such as β-diketonates or EDTA. However, recently several nitrogen-bonded complexes have been well characterized. As with oxygen-donor ligands, amine complexes are generally more stable for chelating ligands. For example, pyridine complexes exist only in solution, while complexes with ethylenediamine or 1,10-phenanthroline can be isolated.[1] In addition, Forsberg and co-workers have recently added compounds of the type $Ln(tren)X_3$ [tren = $N(CH_2CH_2NH_2)_3$] and $Ln(tren)_2X_3$ to the list of lanthanide amine complexes.[2,3] We are interested in the structures of these compounds and their possible use as template compounds in macrocycle synthesis.

There has been a continuing interest in the use of lanthanide ions as shift reagents in NMR spectroscopy. During the last decade,[4] lanthanide shift reagents have been actively investigated and utilized in simplifying complex NMR spectra. The utility of these compounds has been hampered to some extent by the simplifying assumptions that must be made—including the geometries. It would be extremely interesting to have a substitutionally inert lanthanide complex formed by an amine macrocycle such as can be envisioned from $Ln(tren)_2$ as a precursor. This paper reports the structural chacterization of $[Nd(tren)_2(CH_3CN)](ClO_4)_3$, as the first step in this project.

Experimental Section

Manipulation of moisture-sensitive materials was accomplished with Schlenk techniques and the use of a Vacuum Atmospheres HE-93-A glovebox with recirculating moisture-free argon atmosphere. Elemental analyses were performed by the Microanalytical Laboratory, University of California, Berkeley, CA. Infrared spectra were obtained on a Perkin-Elmer 597 spectrophotometer (Nujol mulls).

Materials. Acetonitrile (CH_3CN) was distilled from P_2O_5; benzene from potassium-benzophenone ketyl. The tren $[N(CH_2CH_2NH_2)_3]$ was extracted from crude triethylenetetramine.[2] Crystalline 16-cyclam was a generous gift from William Smith.[5]

Neodymium perchlorate $[Nd(ClO_3)_3]$ was prepared by addition of excess Nd_2O_3 to 70% $HClO_4$.[6] The excess Nd_2O_3 was removed by filtration and the solution evaporated to dryness. Residual H_2O was removed by heating to ~250 °C under vacuum for 3 days. Some reversion to the oxide was evidenced by the presence of blue among the pink perchlorate. This contaminant was conveniently left behind during an extraction into acetonitrile. Evaporation of the solution left a compound of formula $Nd(ClO_4)_3(CH_3CN)_4$. Anal. Calcd for $Nd(ClO_4)_3(CH_3CN)_4$: C, 15.83; H, 1.98; N, 9.27; Nd, 23.78. Found: C, 16.23; H, 2.26; N, 9.23; Nd, 24.88.

$[Nd(16\text{-}aneN_4)][ClO_4]_3$. The combination of $Nd(ClO_4)_3(CH_3CN)_4$ and 16-cyclam (16-aneN_4) in a 1:2 molar ratio leads to an intractable blue solid that was not characterized. The similar reaction in a 1:1 molar ratio leads to the formation of an acetonitrile-soluble material of formula $[Nd(16\text{-cyclam})](ClO_4)_3$, and single crystals were obtained from CH_3CN solutions. Anal. Calcd for $NdC_{12}H_{24}Cl_3O_{12}N_4$: C, 21.47; H, 4.17; N, 8.35; Nd, 21.51. Found: C, 21.71; H, 4.23; N, 8.80; Nd, 21.11.

For an apparently orthorhombic single crystal, 5355 X-ray diffraction data were collected for $4° \leq 2\theta \leq 55°$. The unit cell size and contents are a = 18.192 (2) Å, b = 15.762 (2) c = 8.096 (1) Å, and Z = 4. Refinements in space group $Pn2_1a$ or its centric alternative $Pnma$ did not lead to a successful solution of the structure, apparently due to a major disorder involving closely related isomers of the cation. Complete solution of this structure has been abandoned, but we are able to report that the Nd^{3+} ion is seven- or eight-coordinate with coordination by four 16-cyclam nitrogen atoms, one oxygen atom from each of two of the perchlorate anions, and one or two oxygen atoms from the remaining perchlorate anion. The Nd–N and Nd–O bond lengths are about 2.5 Å.

$[Nd(tren)_2(CH_3CN)](ClO_4)_3$. This complex, originally reported as $Nd(tren)_2(ClO_4)_3$, was prepared after the method of Forsberg.[3] Crystals suitable for diffraction were obtained by the addition of benzene to a concentrated acetonitrile solution of the complex. After 2 days of standing at room temperature, the clear pink solution yielded several large, well-formed crystals. Infrared spectroscopy revealed the presence of acetonitrile (ν_{CN} = 2262 cm^{-1}).

Data Collection, Solution, and Refinement[7]

The absences identified with the precession camera (hkl, $h + k$

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[1] Cotton, F. A.; Wilkinson, G. W. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 1069.
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Table Ia. Positional Parameters for $[Nd(tren)_2(CH_3CN)](ClO_4)_3$

	x	*y*	*z*		*x*	*y*	*z*
Nd	−0.250000	−0.235763 (17)	0	O(8)	0.0299 (5)	−0.0471 (5)	−0.3472 (8)
Cl(1)	−0.16340 (17)	−0.36018 (14)	−0.5761 (2)	O(9)	−0.4388 (8)	−0.1258 (10)	−0.5321 (8)
Cl(2)	−0.05706 (16)	−0.07716 (15)	−0.3868 (3)	O(10)	−0.4169 (9)	−0.1141 (9)	−0.3288 (8)
Cl(3)	−0.38879 (16)	−0.15158 (13)	−0.4311 (2)	O(11)	−0.4016 (12)	−0.2248 (6)	−0.4150 (13)
N(1)	−0.2693 (4)	−0.3781 (3)	−0.0893 (6)	O(12)	−0.3019 (7)	−0.1364 (10)	−0.4381 (16)
N(2)	−0.4074 (5)	−0.2625 (4)	−0.1225 (6)	C(1)	−0.2191 (6)	−0.3863 (5)	−0.1983 (8)
N(3)	−0.2009 (5)	−0.2504 (4)	−0.2184 (6)	C(2)	−0.1531 (6)	−0.3235 (6)	−0.2122 (9)
N(4)	−0.1339 (5)	−0.3341 (4)	0.0931 (6)	C(3)	−0.3655 (7)	−0.3960 (6)	−0.1191 (9)
N(5)	−0.3521 (4)	−0.1357 (3)	0.1090 (5)	C(4)	−0.4132 (6)	−0.3352 (6)	−0.1904 (8)
N(6)	−0.1767 (5)	−0.1829 (5)	0.2069 (7)	C(5)	−0.2343 (8)	−0.4307 (4)	0.0066 (14)
N(7)	−0.2668 (5)	−0.1045 (4)	−0.1092 (6)	C(6)	−0.1427 (7)	−0.4139 (6)	0.0534 (10)
N(8)	−0.3470 (5)	−0.2967 (4)	0.1601 (6)	C(7)	−0.3000 (7)	−0.0938 (5)	0.2073 (8)
N(9)	−0.0869 (5)	−0.1767 (4)	−0.0183 (7)	C(8)	−0.2025 (10)	−0.1043 (7)	0.2124 (12)
O(1)	−0.1006 (6)	−0.3106 (5)	−0.6216 (8)	C(9)	−0.3890 (6)	−0.0829 (5)	0.0147 (8)
O(2)	−0.2261 (8)	−0.3140 (10)	−0.5198 (17)	C(10)	−0.3206 (7)	−0.0465 (5)	−0.0537 (9)
O(3)	−0.2144 (7)	−0.3973 (5)	−0.6718 (7)	C(11)	−0.4256 (6)	−0.1766 (5)	0.1614 (8)
O(4)	−0.1247 (7)	−0.4066 (5)	−0.4888 (8)	C(12)	−0.3950 (7)	−0.2431 (5)	0.2334 (8)
O(5)	−0.0450 (8)	−0.1462 (8)	−0.4427 (13)	C(13)	−0.0226 (6)	−0.1446 (5)	−0.0283 (7)
O(6)	−0.1082 (6)	−0.0882 (6)	−0.2891 (7)	C(14)	0.0592 (7)	−0.1033 (6)	−0.0405 (10)
O(7)	−0.1003 (6)	−0.0294 (6)	−0.4732 (8)				

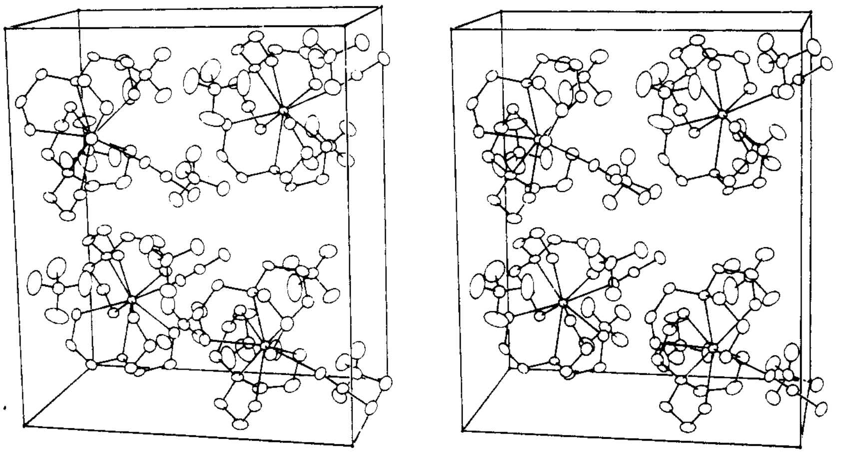

Figure 1. Stereoscopic drawing of the unit cell of $[Nd(tren)_2(CH_3CN)](ClO_4)_3$.

odd; *h*0*l*, *l* odd) are consistent with the space groups *Cc* and *C*2/*c*. The cell parameters were determined with 25 automatically centered reflections with 2θ between 27 and 43°. They are a = 15.0442 (11) Å, b = 17.7290 (14) Å, c = 11.0880 (6) Å, and β = 95.079 (5)°. These data, in conjuction with the measured density (1.751 g cm^{-3}) yield $Z = 4$ (d_{calcd} = 1.750 g cm^{-3}).

Table II. Pertinent Bond Distances (Å) for $[Nd(tren)_2(CH_3CN)](ClO_4)_3$

Nd–N(1)	2.717 (6)	Nd–N(6)	2.629 (7)
Nd–N(2)	2.666 (7)	Nd–N(7)	2.625 (7)
Nd–N(3)	2.607 (6)	Nd–N(8)	2.628 (7)
Nd–N(4)	2.615 (7)	Nd–N(9)	2.692 (7)
Nd–N(5)	2.701 (6)	Nd–N(av)	2.65 (4)
N(1)–C(1)	1.49 (1)	N(5)–C(7)	1.49 (1)
C(1)–C(2)	1.51 (1)	C(7)–C(8)	1.47 (2)
C(2)–N(3)	1.48 (1)	C(8)–N(6)	1.45 (1)
N(1)–C(3)	1.49 (1)	N(5)–C(9)	1.47 (1)
C(3)–C(4)	1.48 (1)	C(9)–C(10)	1.48 (1)
C(4)–N(2)	1.49 (1)	C(10)–N(7)	1.48 (1)
N(1)–C(5)	1.48 (1)	N(5)–C(11)	1.48 (1)
C(5)–C(6)	1.46 (2)	C(11)–C(12)	1.48 (1)
C(6)–N(4)	1.48 (1)	C(12)–N(8)	1.48 (1)
N(9)–C(13)	1.14 (1)	C(13)–C(14)	1.45 (1)
Cl(1)–O(1)	1.416 (8)	Cl(2)–O(5)	1.391 (11)
Cl(1)–O(2)	1.432 (12)	Cl(2)–O(6)	1.396 (7)
Cl(1)–O(3)	1.416 (8)	Cl(2)–O(7)	1.396 (8)
Cl(1)–O(4)	1.361 (8)	Cl(2)–O(8)	1.444 (8)
Cl(3)–O(9)	1.371 (10)	Cl(3)–O(10)	1.412 (10)
Cl(3)–O(11)	1.327 (10)	Cl(3)–O(12)	1.344 (10)

The initial Patterson map confirmed the noncentric space group *Cc*. The structure was then solved by using heavy–atom techniques. The model refined to weighted and unweighted *R* factors of 3.19 and 2.94%, respectively.[9] (The initial polarity refined to 3.58 and 3.24%.) Final positional and thermal parameters appear in Table I.[11] Pertinent bond distances appear in Table II.

Discussion

The crystal structure consists of discrete, mononuclear cations at general positions in the unit cell (Figure 1) engaged

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(7) A total of 3819 +*h*, +*k*, ±*l* data were collected between 4 and 56° in 2θ, (Mo Kα, $\bar{\gamma}$ = 0.71073 Å), monitoring three intensity standards every 7200 s of X-ray exposure and checking three orientation standards every 250 reflections. Azimuthal scans were collected on four reflections with 2θ between 11 and 33°. Further details of data collection, reduction, and processing are described elsewhere.[8] The intensity standards underwent decay of 14, 14, and 17% during data collection. A decay correction of 14% was applied. The six crystal faces were identified with the help of the diffractometer and their dimensions measured at 7× under a binocular microscope. The absorption correction (μ = 21.09 cm^{-1}) applied ranged between 1.212 and 1.498. The data were then average (R = 2.6%) to yield the 3553 independent reflections used in refinement.

(8) Sofen, S. R.; Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 7882.

(9) After a difference Fourier revealed most of the hydrogens, their positions were calculated with a C–H distance of .95 Å and an N–H distance of 0.87 Å.[10] The anisotropic temperature factors of all atoms were refined except for those of the hydrogens, where the isotropics *B*'s were set at 7.0 Å^2 and not refined. On the final least-squares cycle, all parameters shifted by less than 0.06σ. In the final difference Fourier, the largest peak at a grid point was 0.55 e/Å^3 and the most negative electron density was −0.38 e/Å^3. The residuals showed no abnormalities.

(10) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(11) Supplementary material includes tabulations of the refined thermal parameters, the difference between new and old atom positions after rotation by 180° about the pseudo-twofold axis, the intraligand bond angles, and the hydrogen-bonding distances.

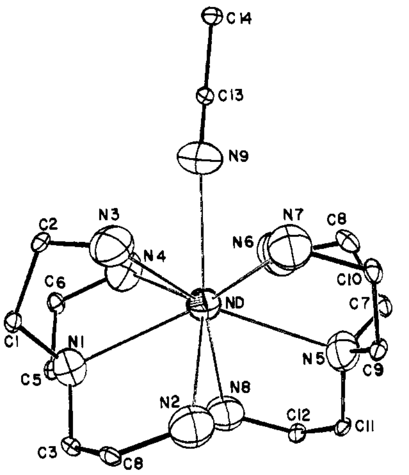

Figure 2. ORTEP drawing of the molecular cation of [Nd(tren)$_2$(CH$_2$CN)](ClO$_4$)$_3$ emphasizing the pseudo-threefold symmetry. The nitrogen atoms are drawn at the 50% contour. For clarity, the carbon atoms are drawn at the 10% contour.

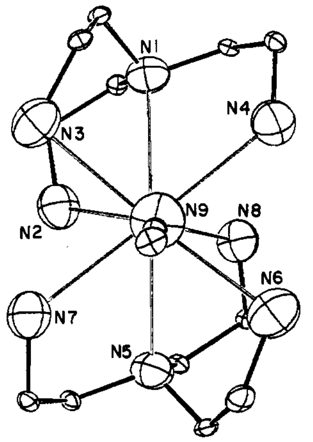

Figure 3. ORTEP drawing of the molecular cation of [Nd(tren)$_2$(CH$_3$CN)](ClO$_4$)$_3$ emphasizing the pseudo-twofold symmetry. The nitrogen atoms are drawn at the 50% contour. For clarity, the carbon atoms are drawn at the 10% contour.

in a three-dimensional network of hydrogen bonds. The structure of the molecular cation (Figure 2) consists of Nd^{3+} coordinated by eight tren nitrogens and an acetonitrile nitrogen to form a tricapped trigonal prismatic coordination geometry. The inclusion of two tetradentate tren ligands in the coordination sphere of one neodymium ion is a reflection of the lanthanide's relatively large size. As in other tren structures (vide infra), the intraligand bond angles indicate the ligand molecule is essentially unstrained.[11] The capping nitrogens are the two tertiary tren nitrogens and that of the acetonitrile. Data on the various planes and their interrelationship can be found in Table III.[11] An idealized tricapped trigonal prism exhibits angles of 0° between end faces, 60° between rectangular faces, and 90° between the two sets of faces. The data in Table III reveal a close resemblance to the idealized polyhedron (see Figure 2) and suggest a molecular (noncrystallographic) twofold axis along the acetonitrile (Figure 3).[11] A twofold axis was then defined as the vector from Nd to a point whose coordinates were obtained by the summation of all pseudo-twofold related atoms (C's and N's). Rotation by 180° about this axis and calculation of the difference between the new atom positions and the old ones defines the quality of the twofold[11] axis. The average difference is 0.21 Å with a standard deviation of 0.16 Å. The major deviations from the twofold symmetry are the carbon atoms of the acetonitrile; the remaining atoms have an average difference of 0.16 Å with a standard deviation of 0.06 Å. When only the nitrogen atoms that constitute the coordination sphere are considered, the average difference is 0.11 Å, with a standard deviation of 0.03 Å.

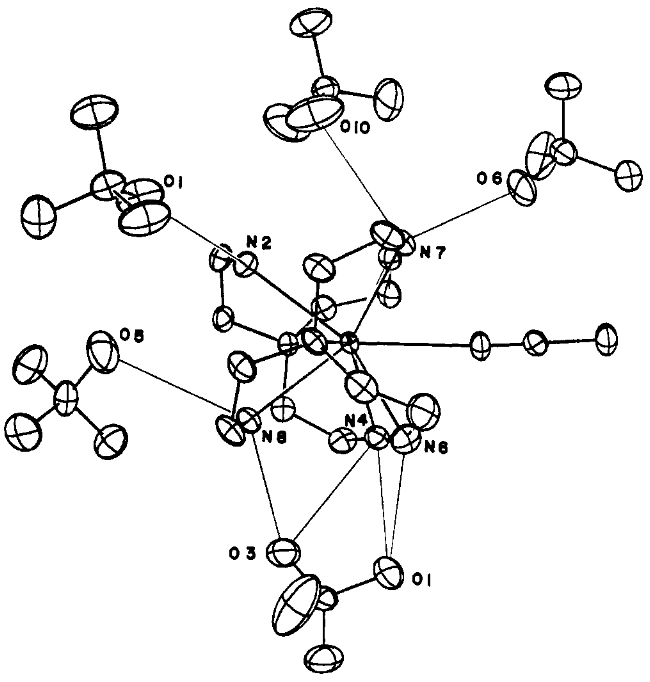

Figure 4. ORTEP drawing of the hydrogen bonding experienced by one molecular cation of [Nd(tren)$_2$(CH$_3$CN)](ClO$_4$)$_3$.

Table IV. Interatomic Distances (Å) for [Nd(tren)$_2$(CH$_3$CN)](ClO$_4$)$_3$

N	dist	N	dist	N	dist
3, 7	3.06	7, 2	3.51	4, 8	3.42
6, 4	3.06	6, 8	3.27	3, 4	3.81
2, 8	3.24	2, 3	3.38	6, 7	3.90

Figure 4 illustrates the hydrogen bonding around a cation and between perchlorate oxygens and some of the primary amine nitrogens. There are eight such bonds within 3.25 Å, ranging from 3.11 to 3.25 Å.[11] Among the other metal tren structures pubished is another example of a perchlorate salt, [Co(tren)(glycinato)]Cl(ClO$_4$), where a more extensive hydrogen-bonding network was found.[12] Of the remaining tren structures that have been reported,[13-16] the ligands in each case are tetradentate.

The compound [Eu(terpy)$_3$](ClO$_4$)$_3$[17] is the only other lanthanide structure determined to date in which all coordination sites are occupied by nitrogen atoms. In this and other mixed-lanthanide amine complexes, the M–N bond distances are in general agreement with those predicted from the metal ionic radii. The M–N distances in [Eu(terpy)$_3$](ClO$_4$)$_3$ are about 0.05 Å shorter than those found in the present compound. This difference is about what one would expect for the difference between an sp^3- and an sp^2-hybridized nitrogen atom (0.08 Å) and the difference in ionic radii of Nd^{3+} and Eu^{3+} ion (0.04 Å).[18]

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(13) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1974**, *13*, 2056.

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(18) Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 276.

The crystal structure was carried out in part to determine the appropriate number of carbon atoms needed to bridge across the tren ligands in order to encapsulate the metal ion. The proposed encapsulation would bridge the closest nitrogens (Table IV): 3 and 7, 6 and 4, and 2 and 8. In the structure of 16-aneN_4,[5] nonbonded nitrogens are separated by 2.9 Å and bridged by propyl chains. This appears to be the appropriate length for an encapsulating reaction.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. W-7405-ENG-48. The Berkeley CHEXRAY facility was established in part from an NSF departmental instrumentation grant.

Registry No. [Nd(tren)$_2$(CH$_3$CN)](ClO$_4$)$_3$, 81293-68-7; [Nd(16-aneN$_4$)][ClO$_4$]$_3$, 81277-15-8; Nd(ClO$_4$)$_3$(CH$_3$CN)$_4$, 81277-16-9.

Supplementary Material Available: Tables of calculated hydrogen atom positions (Table Ib), relationships between planes (Table III), thermal parameters (Table V), ligand bond angles (Table VI), results of a twofold rotation (Table VII), hydrogen bond lengths (Table VIII), structure factors, and general temperature factor expressions (*U*) (55 pages). Ordering information is given on any current masthead page.

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MO Nature of the Collinear M-S-M Bridged Linkages in Dinuclear Thiometal Complexes

Carlo Mealli and Luigi Sacconi*

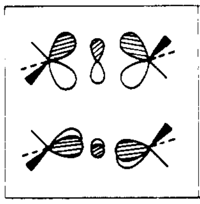
Received February 9, 1981

A few years ago we described two diamagnetic binuclear compounds containing one sulfur atom linearly bridging two metal ions, namely, [(triphos)NiSNi(triphos)](BPh$_4$)$_2$·1.6DMF (A) (triphos = CH$_3$C(CH$_2$PPh$_2$)$_3$) and (np$_3$)CoSCo(np$_3$) (B)[1] (np$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$). In both compounds the metals are pseudotetrahedrally coordinated by three phosphorus atoms of a polyphosphine ligand and by one shared sulfur atom. The M–S linkages are unusually short, being 2.034 Å for Ni–S and 2.128 Å for Co–S. In the absence of detailed MO calculations we then adapted to our cases the old qualitative MO procedure introduced by Orgel and Dunitz for $Ru_2Cl_{10}O^{4-}$.[2] Thus specific symmetry arguments for A (site symmetry D_{3d}) prompted that the bonding network of the molecule is dominated by e_u bonding, nonbonding, and antibonding molecular orbitals, with the last orbitals being too high in energy for them to be populated. This accounted for the quenching of the paramagnetism on each metal center and predicted the formation of π-type bonds between suitable metal d orbitals and sulfur p orbitals of e_u symmetry (d_π–p_π interactions).

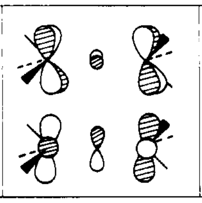
Recently the structure of the compound [(η^5-C$_5$H$_5$)Cr(CO)$_2$]$_2$S (C) has been reported.[3] This complex too has an almost linear Cr–S–Cr linkage for which the authors proposed the Cr≡S≡Cr formulation. In this manner the closed-shell configuration of the metals that start from an initial 15-electron counting is attained.[4] The same authors also suggested that this argument can be conveniently applied to our compounds as well.

We have now reconsidered the matter by a more quantitative MO treatment based on the extended Hückel method. Our aim is to point out the most important orbital interactions in this type of compound and to probe the role of the sulfur d orbitals, which must enter in an overall triple-bonding VB scheme such as that invoked by Greenhough et al.[3]

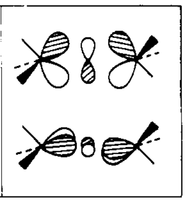
The level ordering in an hypothetical molecule of D_{3d} symmetry such as $[(PH_3)_3Ni\text{–}S\text{–}Ni(PH_3)_3]^{2+}$ with and without the contribution of sulfur d orbitals is shown in Figure 1, parts e and c, respectively. The construction and the shapes of the MO's of a M_2L_6 fragment from two ML_3 units brought together (Figure 1a,b) have been described in detail by Hoffmann and co-workers.[5] Here we remind the readers that the metal d orbitals of e symmetry in the ML_3 units are titled and that there is partial hybridization of d and p metal orbitals in the upper e set. In the M_2L_6 fragment there are two metal e_u sets that can match the e_u (p_x, p_y) orbitals of sulfur. The possible interactions are shown in **1**, **2**, and **3** and correspond to the $1e_u$, $2e_u$, and $3e_u$ orbitals of Figure 1c. It should be noted that, due to the interaction with the sulfur e_u set, the $1e_u$ and $2e_u$ orbitals of the M_2L_6 fragment intermix in a sense so as to reduce the tilting with respect to the metal–metal vector. As an example **4** shows how the upper component of **2** can be built up from three combining e_u members. The $2e_u$ level can be considered metal–sulfur nonbonding and δ metal–metal antibonding. Thus **1**, **2**, and **3** may be closely related to the bonding, nonbonding and antibonding e_u levels first predicted by our MO qualitative description of A. This type of π interaction contributes a value of 0.27 to the Mulliken overlap population of each Ni–S bond. Besides this there are σ-type bonding orbitals that formally allow an overall double-bond VB representation of the Ni=S=Ni linkage. These are the $1a_{1g}$ and $1a_{2u}$ orbitals of Figure 1c centered on sulfur s and p_z orbitals, respectively. The bonding partners of the M_2L_6 fragment are the high-lying $2a_{1g}$ and $2a_{2u}$ metal sp hybrids of Figure 1b. The large energy gaps do not totally prevent the possibility of good bonding interactions. In fact the large overlaps obtainable between the highly diffuse s and p orbitals at short Ni–S distances account for a net σ-type contribution of 0.54 to the overlap population of each Ni–S bond. Interestingly the metal d_{z^2} combinations ($1a_{1g}$ and $1a_{2u}$ of Figure 1b) mix into the Ni–S–Ni bonding network, but their contribution to the Ni–S overlap population is practically vanished,



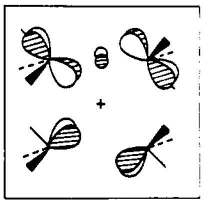
1



2



3



4

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(4) In this electron counting the metal d electrons, calculated by considering the sulfur atom as uncharged, are added to the total number of electrons donated by the terminal ligands.

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