amido nitrogen atom is common to both possible arrangements. This is not necessarily predictable although the obvious rationalization is that the more basic donor set is preferred.

The structure found invites comparison with that of tetrakis(2-amino-6-methylpyridine)dimolybdenum, $Mo_2(map)_4$, which we recently reported.[10] Before doing this it is important to emphasize that most of the interatomic distances and angles determined here cannot be taken as reliable in the usual way, say to $\pm 3\sigma$, because of the effects of the disorder. All that can be said of most of the distances is that the values obtained are reasonable under the circumstances and do nothing to vitiate the assumed model of the disorder.

The only distances that could be expected to have meaningful accuracy are the Mo–Mo′ distance, which should, in fact, be as reliable as the esd of 0.003 Å implies, and, with some qualification, the Mo–N distance. The Mo–N distance, 2.178 (6) Å, is an average of the two chemically different kinds. In $Mo_2(map)_4$ the two kinds had values of 2.18 (1) Å (for pyridine) and 2.14 (1) Å. All things considered, the present value is then a very reasonable one. It was also found in the $Mo_2(map)_4$ structure that the two kinds of Mo′–Mo–N angles, to ring nitrogen and exo nitrogen atoms, had equal average values, viz., 92.9 ± 0.4 and 93.1 ± 0.2°. In the present structure the available value for such angles is 92.8°. It is probable that the close similarity of the intrinsic Mo–N distances and Mo′–Mo–N angles for the two sorts of nitrogen atoms helps make possible the disordered packing of the molecules and also leads to the "almost normal" thermal parameters for the nitrogen atoms despite the disordered structure.

The remarkable feature of this molecule is that it establishes a new record for the shortness of Mo–Mo bonds, 2.037 (3) Å. This is a nontrivial change, viz., 0.027 Å, from the previous record, viz., 2.064 (1) Å, found in tetrakis(2,6-dimethoxyphenyl)dimolybdenum. It may also be compared with the distance in $Mo_2(map)_4$, namely, 2.070 (1) Å. It seems likely that the difference between the present molecule and $Mo_2(map)_4$ is essentially an electronic one, resulting from the replacement of H by CH_3CO on the exo nitrogen atoms, but certainly we cannot offer any explanation of why this causes the Mo–Mo bond to become shorter.

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Registry No. $Mo_2[(C_5NH_4)NC(O)CH_3]_4$, 71097-02-4.

Supplementary Material Available: A table of final calculated and observed structure factors (2 pages). Ordering information is given on any current masthead page.

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Reformulation from X-ray Crystallography of a Dinuclear Thiocyanate Complex of Rhenium. The First Observation of Solely N-Bonded, Bridging Thiocyanate

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We report the correct identification and the crystal structure of $(n\text{-}Bu_4N)_3Re_2(NCS)_{10}$, a compound previously reported with a formula also including two CO groups, $(n\text{-}Bu_4N)_3Re_2(NCS)_8(CO)_2$. The IR bands which afforded the only positive reason for supposing the CO groups to be present are now recognized to arise from CN stretching in N-bridging NCS ligands, a structural element sometimes mentioned but never previously documented. The $[Re_2(NCS)_{10}]^{3-}$ anion consists of two octahedra sharing an edge formed by the nitrogen atoms of bridging NCS ions. The virtual D_{2h} symmetry of the inner Re_2N_{10} set of atoms implies that the unpaired electron in this formally mixed-valence (+3, +4) complex is delocalized equally over both metal atoms. The Re–Re distance of 2.613 (1) Å indicates the existence of a metal–metal bond. The crystals may be assigned to space group $I2/a$ with $a = 24.016$ (8) Å, $b = 14.340$ (2) Å, $c = 24.798$ (5) Å, $\beta = 110.5°$, $V = 7999$ (3) Å^3, and $Z = 4$. The structure has been refined to discrepancy indices of $R_1 = 0.043$ and $R_2 = 0.060$ by using 3663 reflections with $I > 3\sigma(I)$ collected on a spherical crystal.

Introduction

In 1966, in the course of some of the earliest investigations[2] of the chemical reactivity of quadruple bonds, there was found among the products of the reaction of sodium thiocyanate with $(n\text{-}Bu_4N)_4Re_2Cl_8$ a substance for which the formula $(n\text{-}Bu_4N)_3Re_2(NCS)_{10}(CO)_2$ was suggested. This suggestion rested primarily on two pieces of evidence. First, strong bands in the infrared spectrum at ca. 1920 and ca. 1885 cm^{-1} were taken to indicate the presence of two CO groups (presumed to have been derived from the reaction solvent, acetone). This postulate was considered necessary since there was no known form of coordinated thiocyanate ion giving rise to strong infrared bands in that frequency range. Second, the proposed formula agreed with analytical data. Magnetic and conductance measurements were also consistent with this formula, of which the pertinent features are an odd number of electrons and a 3:1 cation to anion ratio, respectively.

The formula $(n\text{-}Bu_4N)_3Re_2(NCS)_{10}(CO)_2$ has, however, always seemed somewhat overendowed with ligands and, on that ground, questionable. Proof of its correctness through

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X-ray crystallography has not been given for the practical reason that no suitable crystals had previously been grown. Recently, however, some very large, well-formed crystals were obtained and it seemed worthwhile and indeed highly desirable to determine conclusively whether the proposed formula is correct.

We report here that X-ray crystallography shows that there are no CO groups present and that the strong infrared bands are to be assigned to two bridging NCS^- ions of a type never before observed, in spite of the enormous amount of information available on the protean coordinating capabilities of the NCS^- ion.[3]

Experimental Section

The compound was prepared in the manner previously described.[2] Large crystals were obtained in 33% overall yield by adding ether to an acetonitrile solution and chilling to −10 °C.

X-ray Data Collection. One of the large crystals of $[n\text{-}Bu_4N][Re_2(NCS)_{10}]$ was ground to a sphere with a diameter of 0.35 mm and used for preliminary examination and data collection. It was secured to the end of a thin glass fiber with epoxy cement and mounted on a Syntex $P\bar{1}$ automatic diffractometer.

Preliminary rotation and oscillation photographs indicated that the crystal was monoclinic and examination of selected reflections indicated that it was a single crystal of good quality. ω scans showed that several intense reflections had widths at half-height of less than 0.3°. Examination of data collected in a preliminary data set showed absences hkl, $h + k + l = 2n + 1$, and $h0l$, $h = 2n + 1$, consistent with the space group $I2/a$, which though nonstandard proved very satisfactory. Careful centering of 15 reflections in the range $25 < 2\theta < 33°$ gave unit cell parameters $a = 24.016$ (6) Å, $b = 14.340$ (2) Å, $c = 24.798$ (5) Å, $\beta = 110.5°$, and $V = 7999$ (3) Å^3. This volume is consistent with $Z = 4$. The procedures preliminary to data collection have been described previously.[4]

All data were collected by using Mo Kα (λ 0.71073 Å) radiation monochromatized in the incident beam with a graphite crystal. A total of 4263 independent reflections with $0 < 2\theta < 45°$ were collected at 22 ± 4 °C by using the θ–2θ scan technique. A variable scan rate from 4 to 24° min^{-1} was used with a scan range of Kα_1 − 1.0° to Kα_2 + 1.0° and a scan to background time ratio of 2. The intensities of three standard reflections were measured after every 97 reflections and showed no significant variation during the period of data collection. Lorentz and polarization corrections were applied.[5] The linear absorption coefficient for the crystal is $\mu = 34.88$ cm^{-1}. A spherical absorption correction (minimum = 2.35, maximum = 2.39, average = 2.37) was applied to the data.

Solution and Refinement.[5] The structure was solved in the monoclinic space group $I2/a$. The position of the independent rhenium atom was found by solution of the three-dimensional Patterson function. Subsequent Fourier and difference syntheses gave the positions of the remaining atoms. Full-matrix anisotropic least-squares refinement of all atomic positional parameters and temperature factors gave final discrepancy indices of

$$R_1 = (\sum||F_o| - |F_c||)/\sum|F_o| = 0.043$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.060$$

and a goodness of fit parameter of 1.295. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. Atomic scattering factors were those of Cromer and Waber.[6] Anomalous dispersion effects were included in the scattering factors of rhenium. A table of observed and calculated structure factors is available as supplementary material.

Results

The atomic positional and thermal parameters are given in Table I. A computer-generated drawing of the $[Re_2(NCS)_{10}]^{3-}$ anion, in which the atomic numbering scheme is defined, is shown in Figure 1. The bond lengths and angles are listed in Tables II and III, respectively. Figure 2 gives schematic drawings in which the atom numbers for the two crystallographically independent tetra-n-butylammonium ions are given.

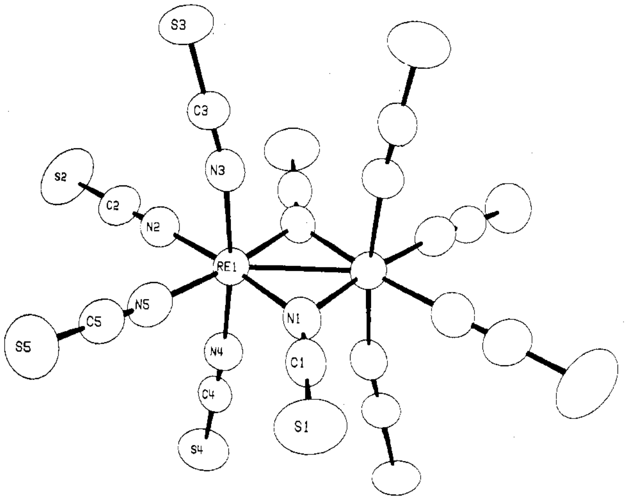


Figure 1. A computer-generated drawing of the $[Re_2(NCS)_{10}]^{3-}$ ion showing the numbering system. Unlabeled atoms may be denoted by primed numbers corresponding to those of the atoms to which they are related by a center of inversion.

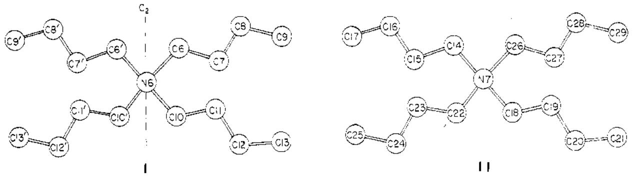


Figure 2. Schematic diagram of the two n-butylammonium ions. The figure is not intended to depict the actual geometry of the ions but only the atoms associated with the n-butylammonium cations. I sits on a crystallographic twofold axis of symmetry while II occupies a general position.

The $[Re_2(NCS)_{10}]^{3-}$ ions are located on crystallographic inversion centers. The ion consists of two distorted octahedra sharing an edge formed by the nitrogen atoms of two bridging NCS ions. The remaining vertices of each octahedron are also occupied by nitrogen atoms. The anion as a whole has approximate D_{2h} symmetry. Each NCS ligand, including the bridging ones, is effectively linear; angles at the carbon atoms range from 177.8 to 179.6°. For the four terminal ligands the Re–N–C angles range from 165.4 to 176.4°. The bridging NCS ligands are essentially perpendicular to the Re–Re′ axis with an Re–N–Re′ angle of 77.4°. The Re–Re′ distance of 2.613 (1) Å is indicative of a bond, though not a strong one.

Of the 12 $[(n\text{-}C_4H_9)_4N]^+$ ions in the unit cell, eight reside on general positions and four on twofold axes. The distances and angles within these ions are all normal and require little comment. The scatter in the N–C and C–C distances and in the N–C–C and C–C–C angles doubtless arises from the considerable thermal motion, which is quite a common feature of $[(n\text{-}C_4H_9)_4N]^+$ ions in most crystals.

Discussion

The structure now found for this compound can, happily, account for all of the experimental data reported earlier. The elemental analysis satisfies the correct formula as well as it does that previously suggested, as shown in Table IV. The infrared absorptions at ca. 1900 cm^{-1} must be assigned to ν(C–N) in the bridging isothiocyanate ions. This is a situation for which there was no precedent at the time this complex was first reported nor is there any even today (see below). Hence, prior to the determination of this structure, there had been no clue as to the true significance of the infrared bands at ca. 1900 cm^{-1}, and that is why they were, incorrectly, thought to indicate the presence of terminal CO ligands.

A centrosymmetric structure would be expected to have only one such band and the appearance of two, even in solution, requires some comment. As far as the crystal spectrum is concerned intermolecular coupling could provide an expla-

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re(1)	0.02119 (2)	0.04530 (3)	0.04867 (2)	5.14 (1)	3.85 (1)	4.02 (1)	−0.88 (2)	1.70 (1)	−0.18 (2)
S(1)	0.1640 (1)	−0.1615 (3)	0.0424 (2)	7.1 (1)	7.2 (2)	10.8 (2)	1.1 (1)	3.4 (1)	1.8 (2)
S(2)	−0.0479 (2)	0.2783 (3)	0.1480 (2)	9.5 (2)	7.1 (2)	12.9 (2)	−0.2 (1)	6.1 (1)	−3.2 (1)
S(3)	0.0813 (1)	0.3296 (2)	−0.0139 (1)	6.2 (1)	4.1 (1)	7.2 (1)	−0.4 (1)	1.5 (1)	1.3 (1)
S(4)	−0.0495 (1)	−0.1692 (2)	0.1569 (1)	7.4 (1)	7.1 (2)	7.3 (1)	−0.8 (1)	3.51 (9)	2.1 (1)
S(5)	0.2144 (1)	0.0700 (3)	0.1920 (1)	5.7 (1)	8.7 (2)	7.3 (2)	−0.6 (1)	1.1 (1)	−0.8 (1)
N(1)	0.0632 (3)	−0.0549 (5)	0.0152 (3)	4.6 (3)	4.6 (4)	3.7 (3)	−1.1 (3)	1.0 (2)	−0.1 (3)
N(2)	−0.0106 (3)	0.1418 (6)	0.0894 (3)	5.0 (3)	5.1 (4)	4.8 (3)	−1.0 (3)	1.8 (2)	−0.1 (3)
N(3)	0.0497 (3)	0.1560 (5)	0.0141 (3)	5.4 (3)	5.1 (4)	4.0 (3)	−0.6 (3)	1.3 (3)	−0.1 (3)
N(4)	−0.0073 (3)	−0.0519 (5)	0.0919 (3)	6.3 (3)	4.5 (4)	4.4 (3)	−0.7 (3)	2.1 (2)	0.2 (3)
N(5)	0.1011 (4)	0.0501 (5)	0.1144 (3)	6.2 (4)	4.5 (4)	5.7 (4)	−0.8 (3)	2.2 (3)	−0.3 (3)
N(6)	0.2500 (0)	0.3549 (8)	0.5000 (0)	3.7 (4)	6.0 (6)	4.9 (4)	0	1.7 (3)	0
N(7)	0.5896 (3)	0.0669 (5)	0.6492 (3)	5.1 (3)	4.8 (4)	5.5 (3)	0.5 (3)	2.1 (3)	0.7 (3)
C(1)	0.1059 (4)	−0.1014 (7)	0.0267 (4)	5.6 (4)	5.1 (5)	4.1 (4)	−0.9 (4)	2.0 (3)	−0.5 (4)
C(2)	−0.0260 (4)	0.1992 (7)	0.1142 (4)	5.5 (4)	4.6 (5)	6.3 (5)	−0.8 (4)	2.2 (3)	−0.3 (4)
C(3)	0.0621 (4)	0.2292 (6)	0.0027 (4)	4.4 (4)	4.0 (4)	4.6 (4)	−0.4 (4)	1.0 (3)	0.5 (3)
C(4)	−0.0249 (4)	−0.1014 (7)	0.1192 (4)	5.1 (4)	4.5 (4)	3.6 (4)	0.3 (4)	0.7 (3)	−0.1 (3)
C(5)	0.1496 (4)	0.0592 (6)	0.1471 (4)	5.5 (4)	4.3 (4)	5.1 (4)	−0.5 (4)	2.6 (3)	−0.1 (3)
C(6)	0.3035 (4)	0.4166 (7)	0.5339 (4)	4.2 (4)	6.0 (5)	5.3 (4)	−1.2 (4)	1.4 (3)	−0.3 (4)
C(7)	0.2902 (5)	0.4819 (8)	0.5769 (5)	6.0 (5)	8.1 (6)	6.8 (5)	−2.4 (5)	2.4 (4)	−3.3 (5)
C(8)	0.3413 (5)	0.5446 (8)	0.6057 (5)	7.1 (5)	7.2 (6)	6.7 (5)	−1.8 (5)	2.1 (4)	−1.6 (5)
C(9)	0.3299 (7)	0.6114 (11)	0.6475 (6)	10.4 (8)	11.1 (9)	9.4 (7)	−3.0 (8)	3.9 (6)	−4.0 (7)
C(10)	0.2707 (4)	0.2952 (7)	0.4593 (4)	5.4 (4)	5.1 (5)	5.9 (4)	0.7 (4)	2.7 (3)	−1.0 (4)
C(11)	0.2246 (5)	0.2248 (8)	0.4253 (4)	6.5 (5)	6.5 (5)	6.2 (5)	−0.3 (5)	2.3 (4)	−2.4 (4)
C(12)	0.2512 (5)	0.1681 (9)	0.3894 (5)	7.0 (6)	8.0 (7)	8.0 (6)	−0.5 (6)	1.9 (5)	−2.8 (5)
C(13)	0.2129 (6)	0.0832 (10)	0.3604 (6)	8.7 (7)	8.5 (7)	8.3 (6)	−0.6 (6)	2.3 (5)	−4.2 (5)
C(14)	0.6251 (5)	−0.0191 (6)	0.6765 (4)	5.8 (5)	3.6 (4)	6.0 (5)	1.0 (4)	1.7 (4)	1.3 (4)
C(15)	0.5951 (6)	−0.1113 (8)	0.6501 (5)	11.1 (7)	4.6 (5)	6.5 (5)	0.4 (5)	2.8 (5)	0.1 (5)
C(16)	0.6358 (6)	−0.1942 (8)	0.6833 (5)	14.0 (8)	4.2 (5)	8.5 (6)	2.2 (5)	5.8 (5)	1.4 (5)
C(17)	0.6318 (7)	−0.2062 (10)	0.7420 (6)	11.9 (8)	8.4 (8)	8.2 (6)	0.5 (7)	3.8 (6)	2.5 (6)
C(18)	0.6263 (5)	0.1491 (7)	0.6814 (5)	6.3 (5)	4.2 (5)	7.4 (5)	0.7 (4)	2.2 (4)	0.1 (4)
C(19)	0.6010 (6)	0.2423 (8)	0.6618 (6)	10.6 (8)	4.3 (5)	10.7 (8)	0.3 (6)	3.4 (6)	1.3 (6)
C(20)	0.6420 (9)	0.3213 (10)	0.6922 (8)	18 (2)	5.8 (7)	11 (1)	−0.8 (9)	0 (1)	0.6 (7)
C(21)	0.6619 (12)	0.3230 (13)	0.7511 (9)	28 (2)	7.4 (9)	16 (1)	1 (1)	6 (1)	3 (1)
C(22)	0.5775 (5)	0.0715 (8)	0.5826 (4)	6.1 (4)	8.0 (7)	5.6 (4)	1.0 (5)	3.0 (3)	1.1 (4)
C(23)	0.6336 (5)	0.0726 (8)	0.5668 (5)	8.9 (5)	6.4 (6)	8.7 (5)	1.6 (5)	5.3 (4)	2.1 (5)
C(24)	0.6113 (6)	0.0858 (10)	0.5002 (5)	9.9 (7)	8.8 (7)	5.6 (5)	0.2 (6)	3.6 (4)	0.5 (5)
C(25)	0.6647 (7)	0.0762 (13)	0.4792 (7)	13.0 (8)	12 (1)	12.2 (7)	2.5 (8)	8.4 (5)	1.0 (8)
C(26)	0.5261 (4)	0.0657 (8)	0.6518 (5)	5.1 (4)	7.5 (6)	7.4 (5)	0.1 (4)	3.1 (3)	0.8 (5)
C(27)	0.5238 (5)	0.0598 (8)	0.7117 (5)	6.0 (5)	8.0 (7)	6.9 (5)	−0.1 (5)	3.0 (4)	0.9 (5)
C(28)	0.4573 (5)	0.0560 (9)	0.7054 (5)	6.8 (5)	9.8 (8)	7.5 (5)	1.6 (6)	3.2 (4)	2.4 (6)
C(29)	0.4464 (7)	0.0524 (12)	0.7589 (6)	9.9 (7)	15 (1)	6.3 (5)	2.4 (8)	3.7 (5)	2.6 (7)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table II. Bond Distances

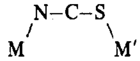
Re(1)-Re(1)	2.613 (1)	N(7)-C(14)	1.52 (1)
N(1)	2.087 (8)	C(18)	1.52 (1)
N(1)′	2.095 (8)	C(22)	1.58 (1)
N(2)	2.015 (9)	C(26)	1.55 (1)
N(3)	2.034 (8)	C(6)-C(7)	1.53 (1)
N(4)	2.018 (8)	C(7)-C(8)	1.49 (1)
N(5)	2.038 (9)	C(8)-C(9)	1.51 (2)
S(1)-C(1)	1.57 (1)	C(10)-C(11)	1.52 (1)
S(2)-C(2)	1.60 (1)	C(11)-C(12)	1.50 (1)
S(3)-C(3)	1.609 (9)	C(12)-C(13)	1.54 (2)
S(4)-C(4)	1.60 (1)	C(14)-C(15)	1.54 (1)
S(5)-C(5)	1.57 (1)	C(15)-C(16)	1.58 (2)
N(1)-C(1)	1.17 (1)	C(16)-C(17)	1.50 (2)
N(2)-C(2)	1.16 (1)	C(18)-C(19)	1.48 (1)
N(3)-C(3)	1.15 (1)	C(19)-C(20)	1.52 (2)
N(4)-C(4)	1.16 (1)	C(20)-C(21)	1.37 (2)
N(5)-C(5)	1.17 (1)	C(22)-C(23)	1.53 (1)
N(6)-C(6)	1.54 (1)	C(23)-C(24)	1.56 (2)
N(6)-C(10)	1.53 (1)	C(24)-C(25)	1.55 (2)
		C(26)-C(27)	1.51 (2)
		C(27)-C(28)	1.55 (2)
		C(28)-C(29)	1.44 (2)

nation. The appearance of two bands in the solution spectrum could have several causes, including the occurrence of ion pairs of lower symmetry, inherent distortion of the central four-membered ring from strict planarity when free of the crystal environment, or, perhaps, Fermi resonance with an overtone of suitable frequency and symmetry type.

The terminal NCS ligands in this structure conform to the usual structural pattern.[7-18] The near linearity of each Re–N–C–S group and the short N–C distances (which average 1.16 (1) Å in this case) are indicative of an electron distribution like that represented by formal structure **1**. The C–S distances, however, are too short, 1.59 (1) Å on average, to be consistent with the C–S single bond implied by **1**. As often suggested before, this may perhaps be explained by some C–S pπ–dπ interaction. Whatever the explanation, it is entirely typical for terminal NCS ligands.

$M \leftarrow N \equiv C{-}S^-$

1



2

The type of bridging NCS ligand found here has no genuine precedent.[3] There are only three cases in which the nitrogen atom of a thiocyanate ion is flanked by two metal atoms in a broadly similar way,[7,8,19] but in each case this seems to be mainly the result of ionic packing. Thus, in [Cu(1,3-diaminopropane)$_2$](NCS)(ClO$_4$),[7] the square CuN$_4$ units are linked through the nitrogen atoms of interleaved NCS$^-$ ions by very long (2.73 Å) Cu–N distances. In the alkali metal–macrocycle complex, [K$_2$C$_{24}$H$_{32}$O$_8$](NCS)$_2$,[8] the pairs of K$^+$ ions are spanned by weakly attached (K–N = 2.84, 2.89 Å) NCS$^-$ ions. In the case of Sn(NCS)$_2$[19] there are pairs of Sn^{2+} ions close to N atoms of half of the NCS$^-$ ions, but there are also several close Sn···S contacts, and the whole ar-

Table III. Bond Angles

Re(1)'-Re(1)-N(1)	51.4 (2)	C(14)-N(7)-C(18)	105.3 (7)
N(1)'	51.2 (2)	C(22)	111.7 (7)
N(2)	135.3 (2)	C(26)	112.3 (7)
N(3)	94.5 (2)	C(18)-N(7)-C(22)	112.2 (7)
N(4)	93.0 (2)	C(26)	112.7 (7)
N(5)	135.1 (2)	C(22)-N(7)-C(26)	102.8 (7)
N(1)-Re(1)-N(1)'	102.7 (3)	S(1)-C(1)-N(1)	178.7 (8)
N(2)'	84.1 (3)	S(2)-C(2)-N(2)	179 (1)
N(3)	95.1 (3)	S(3)-C(3)-N(3)	177.8 (9)
N(4)	92.1 (3)	S(4)-C(4)-N(4)	179.6 (8)
N(5)	83.7 (3)	S(5)-C(5)-N(5)	178.9 (9)
N(2)-Re(1)-N(3)	85.3 (3)	N(6)-C(6)-C(7)	113.1 (7)
N(4)	87.1 (3)	C(6)-C(7)-C(8)	111.4 (9)
N(5)	89.5 (3)	C(7)-C(8)-C(9)	113 (1)
N(3)-Re(1)-N(4)	171.9 (3)	N(6)-C(10)-C(11)	113.3 (7)
N(5)	87.1 (3)	C(10)-C(11)-C(12)	108.0 (8)
N(4)-Re(1)-N(5)	89.9 (3)	C(11)-C(12)-C(13)	113 (1)
Re(1)-N(1)-Re(1)'	77.4 (3)	N(7)-C(14)-C(15)	113.8 (8)
C(1)	143.0 (7)	C(14)-C(15)-C(16)	108.3 (9)
C(1)'	140.0 (7)	C(15)-C(16)-C(17)	110.8 (1.0)
Re(1)-N(2)-C(2)	176.4 (8)	N(7)-C(18)-C(19)	115.6 (9)
Re(1)-N(3)-C(3)	165.4 (7)	C(18)-C(19)-C(20)	113 (1)
Re(1)-N(4)-C(4)	174.1 (7)	C(19)-C(20)-C(21)	118 (2)
Re(1)-N(5)-C(5)	171.2 (8)	N(7)-C(22)-C(23)	114.4 (9)
C(6)-N(6)-C(6)	110 (1)	C(22)-C(23)-C(24)	105 (1)
C(10)	106.2 (5)	C(23)-C(24)-C(25)	109 (1)
C(10)'	111.2 (5)	N(7)-C(26)-C(27)	114.8 (9)
C(10)-N(6)-C(10)	112 (1)	C(26)-C(27)-C(28)	107.2 (9)
		C(27)-C(28)-C(29)	115 (1)

Table IV. Analytical Data (%)

		calcd	
atom	obsd[a]	$(n\text{-}Bu_4N)_3\text{-}Re_2(NCS)_{10}\text{-}(CO)_2$	$(n\text{-}Bu_4N)_3\text{-}Re_2(CN)_{10}$
H	6.51	6.27	6.91
C	41.7	41.50	41.25
N	10.6	10.48	10.78
S	18.0	18.46	18.99

[a] Averages of experimental values reported in ref 2.

rangement is essentially the result of best packing of ions rather than of discrete covalent bonds.

In all known cases of bi- or polynuclear transition-metal complexes[3] with bridging thiocyanate ions, the bridges are bonded to one metal atom by nitrogen and to the other by sulfur, as depicted schematically in **2**.[20,21] The arrangement found here is unique among transition-metal complexes, although the closely similar azide ion is known[22] to form bridges in the same way.

The linearity and distances (N–C = 1.17 (1) Å, C–S = 1.57 (1) Å) in the bridge scarcely distinguish it from the terminal ones. While for the terminal ones the N–C but not the C–S distance could be easily correlated with a simple Lewis structure, **1**, the bridging thiocyanate presents the opposite problem. The "obvious" Lewis structure for a bridging NCS^- ion of the type we have here would seem to be **3**. This provides

$$^{-}\,\ddot{N}{=}C{=}S$$

3

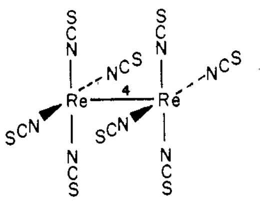
for linearity, directs electron pairs on the nitrogen atom toward the metal atoms, and is consistent with the double bond between the C and S atoms. However, the N–C distance of 1.17 (1) Å is too short for a double bond; it would be more consistent with the triple bond, as in **1**.

The Re–N distances are longer to the bridging nitrogen atoms, 2.091 (8) Å, than to the terminal ones, 2.026 (9) Å (average), which is reasonable and expected.

The Re–Re distance of 2.613 (1) Å and the bridging angles of 102.7 (3)° for N–Re–N and 77.4 (3)° for Re–N–Re clearly indicate direct bonding but it is not obvious what degree of bonding ought to be assumed. Beginning with two octahedra, one with a d^4 ion and the other with a d^3 ion, one can readily imagine a σ bond and a π bond being formed by overlap of appropriate pairs of what would be t_{2g} orbitals in each of the idealized octahedra. The disposition of the remaining three electrons would then be uncertain. The previously reported magnetic properties do not clearly indicate the number of unpaired electrons in view of the large spin–orbit coupling for the rhenium atoms.

Relation to Other Dirhenium Complexes

The range of structures adopted by dirhenium thiocyanate complexes, depending on small changes in oxidation number or ligand content, is quite remarkable. The $[Re_2(NCS)_8]^{2-}$ ion, containing only Re^{III}, is believed to have the quadruply bonded structure **4** (though no crystallographic study has been reported). By simple addition of two phosphine ligands, a structure of type **5** is produced, in which there is no Re–Re bond, as Nimry and Walton[23] have shown. It is worth noting that the conversion of **4** to **5** gives some idea of the strength of the Re–Re quadruple bond in comparison to metal–ligand bonds. In the transformation of **4** to **5** the Re–Re quadruple bond is lost but four new metal–ligand bonds, two Re–P and two Re–S, are formed. Thus, if the reaction of **4** to give **5** is approximately thermoneutral, and if the strengths of the Re–N bonds are about the same in both species, one might conclude that the energy of the Re–Re quadruple bond in **4** is about equal to the sum of two Re–S and two Re–P bond energies.



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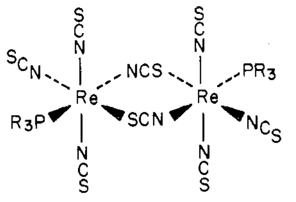

5

The $[Re_2(NCS)_{10}]^{3-}$ ion, in which, again, two additional ligands have been added to **4** but, also, one electron has been removed, is now seen to have still another structure, one in which a significant amount of Re–Re bonding remains.

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Registry No. $(n\text{-}Bu_4N)_3Re_2(NCS)_8(CO)_2$, 12171-33-4; $(n\text{-}Bu_4N)_3Re_2(NCS)_{10}$, 71250-44-7.

Supplementary Material Available: A table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Electrochemical and Spectral Investigations of Nickel(II) Ion Equilibria in Room-Temperature Chloroaluminate Solvents

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Absorption spectra have been recorded for $NiCl_2$ dissolved in 0.8:1 and 1.5:1 molar ratio $AlCl_3$–1-butylpyridinium chloride at room temperature. In basic (chloride-rich) melts, the Ni(II) is present as $NiCl_4^{2-}$, with molar extinction coefficients $a_{658} = 169$ and $a_{705} = 175$ L mol^{-1} cm^{-1}. The reduction of the Ni(II) ion species at vitreous carbon electrodes exhibited irreversible behavior in acidic melts, but no $NiCl_4^{2-}$ ion reduction was detected in the basic solvent. Potentiometry gave a theoretical two-electron Nernst slope for Ni(II) additions in the acidic region and a fourth-power Cl^- ion dependence consistent with $NiCl_4^{2-}$ formation in the basic region. At 40 °C, the Ni(0)/Ni(II) standard electrode potential on the mole fraction scale was determined to be +0.800 ± 0.005 V (vs. a 2:1 Al reference), and an equilibrium constant for the dissociation reaction $NiCl_4^{2-} \rightleftarrows Ni^{2+} + 4Cl^-$ was determined to be $(1.2 \pm 1.0) \times 10^{-46}$.

Introduction

Certain molten salt mixtures of aluminum chloride and alkylpyridinium halides are liquid at ambient temperatures in a broad compositional range, thereby providing unusual ionic solvents for studies of acid–base chemistry, ion complexation, electrochemically generated organic compounds, etc. (e.g., see ref 1–4). A potentiometric investigation of the aluminum species equilibria in $AlCl_3$–1-butylpyridinium chloride (1-BPC) melts[1] has established that the equilibrium constant for solvolysis reaction 1 has a value of $K_3 \lesssim 3.8 \times 10^{-13}$ at 30 °C,

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \qquad (1)$$

the limit arising because the 1-butylpyridinium cation is spontaneously reduced by elemental aluminum in the basic composition range (i.e., <1:1 $AlCl_3$–1-BPC). The extent of formation of the $Al_2Cl_7^-$ ionic species was found to be decidedly enhanced in $AlCl_3$–1-BPC melts over that existing in the higher temperature $AlCl_3$–alkali metal chloride systems for a particular temperature. Additionally, the main disadvantage of the high Al_2Cl_6 vapor pressure found with the acidic $AlCl_3$–alkali metal chloride systems seems to be negated in the corresponding organic halide melts. Further substantiation of these conclusions has come from potentiometric studies made with a metal which is not capable of reducing the pyridinium cation, namely, nickel. Gilbert and Osteryoung[5] have investigated the electrochemistry of Ni(II) species in the $NaAlCl_4$ melt at temperatures between 175 and 210 °C. The Ni(II) standard potential at 175 °C in a melt of pCl^- 5.8 was found to be $E_0 = 1.433 \pm 0.002$ V vs. an Al reference (NaCl saturated). de Fremont et al.[6] have reported a half-wave potential value for Ni(II) ion reduction ($E_{1/2} = +0.83$ V vs. an Al reference (60:26:14)) in the eutectic fused salt $AlCl_3$–NaCl–KCl (60:26:14 mol %) at 140 °C and have found that Ni(II), Co(II), and Fe(II) ion reductions at the DME are irreversible, with a cathodic transfer coefficient for Ni(II) of $\alpha = 0.88$. The Ni–$NiCl_2$ electrode has been tried as a cathode for a solid-electrolyte battery, at operating temperatures of 600–1000 °C.[7]

Results and Discussion

Absorption Spectra. Anhydrous $NiCl_2$ was soluble in basic (<1:1 $AlCl_3$–1-BPC) and, with difficulty, in acidic (>1:1 $AlCl_3$–1-BPC) melts, the basic solutions being sea green/blue and the acidic solutions sandy colored. A light colored precipitate sometimes formed when the acidic melts were allowed to stand. Figure 1a illustrates the optical absorption spectrum of a dilute solution of $NiCl_2$ dissolved in a 0.8:1 melt at room temperature. The spectrum appears to be intermediate to those obtained from $NiCl_4^{2-}$ ions dissolved in pyridinium chloride at 160 °C and that obtained from those ions present as a solid solution in Cs_2ZnCl_4 at room temperature.[8] Absorption spectra of nickel ionic species in molten chloride media have been studied extensively[8-11] and, on the basis of these data, an unambiguous assignment for the spectrum in Figure 1a to a (approximately) tetrahedrally coordinated tetrachloronickelate ion species is possible. The most intense absorption doublet at 705 and 658 nm and the shoulder at ~617 nm (Figure 1a) have been assigned to the spin-allowed absorption $^3T_1(F)$ $^3T_1(P)$.[8-10] For the $NiCl_2$ composition range 1×10^{-3} to 1×10^{-2} M, the Bouger–Beer law was obeyed within experimental error, and molar extinction coefficients for the 658- and 705-nm band maxima computed from the least-squares straight lines were 169 and 175 L mol^{-1} cm^{-1}, respectively. These molar absorptivities are consistent with those of Smith, Liu, and Griffiths[9] for $NiCl_2$/tri-1-butylbenzylphosphonium chloride systems. They reported that increasing temperature (22–172 °C) caused a blue shift in the band maxima and a decrease in absorbance values such that at room temperatures $A_{707} > A_{660}$, whereas both maxima had the same a value of 156 L mol^{-1} cm^{-1} at 172 °C.

Figure 1b illustrates the spectrum of $NiCl_2$ dissolved in an acidic melt; a weak band at ~547 nm was the only band detected in the 400–800-nm spectral range. Øye and Gruen[12] have studied the absorption spectra of dipositive nickel in molten Al_2Cl_6 at 227 °C and 5.6 atm. The spectrum exhibited bands at 476, 926, and 1563 nm which have been interpreted in terms of octahedral coordination of chlorides about the central metal ion. Temperature-dependent equilibria involving

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