Table V. Geometric Factors for Proximal ($H_{1,3}$) and Distal ($H_{2,4}$) Protons[a] of α-$Mo_2Cl_4(LL')_2$

LL′		r, Å	θ, deg	$10^{-27}G$,[b] m^3	$10^{-27}G_{av}$,[b] m^3
dppe	H_1	3.72	105.7	5.03	4.39
	H_3	3.98	71.8	3.75	
	H_2	4.73	104.1	2.59	2.59
	H_4	4.77	76.8	2.59	
dpdt	H_1	3.88	107.6	4.14	4.76
	H_3	3.63	73.9	5.37	
	H_2	4.64	102.9	2.85	2.83
	H_4	4.59	75.6	2.81	

[a] The C–H distance is 1.0 Å, and the C–C–H angle is 109°. [b] $G = (1 - 3\cos^2\theta)/3\gamma^3$.

bond. The opportunity here is actually superior to those in other cases in the sense that there need be no concern with averaging over the rotational space available to the methyl group, as was the case in all earlier estimates of Mo–Mo bond anisotropies.

We wish to apply eq 1, which pertains to the case of axial symmetry.[17,19] Here r is the distance of the test nucleus from

$$\Delta\sigma = \chi(4\pi)(1 - 3\cos^2\theta)/3r^3 \qquad (1)$$

the center of the Mo$\overset{4}{-}$Mo bond and θ is the angle between the **r** vector and C_2 axis perpendicular to the Mo–Mo axis. To do this, we had to calculate the positions of the ethylene protons, which could not be accurately determined by X-ray crystallography. This was done by using conventional crystallographic computer codes for calculating the positions of methylene hydrogen atoms. The calculated geometric factors are listed in Table V. From eq 1 and Table V, the observed $\Delta\sigma$ gives $\chi = (-9680 \pm 250) \times 10^{-36}$ m^3/molecule for α-$Mo_2Cl_4(dppe)_2$. Because of the similarity of α-$Mo_2Cl_4(dpdt)_2$ to α-$Mo_2Cl_4(dppe)_2$, χ is estimated by assuming C_{2h} symmetry, resulting in $\chi = (-8800 \pm 250) \times 10^{-36}$ m^3/molecule.

An additional point to consider is that both dppe and dpdt have aryl groups which potentially could exert ring current effects on the ethylene hydrogen atoms. On the basis of the structure of *anti*-α-$Mo_2Cl_4(dpdt)_2$ as observed in the crystal, this effect has been estimated. A ring current shift diagram for a phenyl group[20] was used, and calculated coordinates of protons relative to each aryl ring allowed us to calculate the ring current shift. It was found that one upright aryl group influences only one nearest-neighbor distal proton to give a 0.16 ppm downfield shift (structure **5**). Consequently, even if this effect contributes to the observed shift, the overestimation of the magnetic anisotropy, as given above, is only 12%, and the χ value is still at least $(-7540 \pm 250) \times 10^{-36}$ m^3/molecule.

There have been previous attempts to estimate χ for the Mo$\overset{4}{-}$Mo bond. McGlinchey[17] proffered a rough estimate of -7500×10^{-36} to -12600×10^{-36} m^3/molecule, employing chemical shifts for the ring protons of $Mo_2Br_2(O_2CPh)_2[P(n\text{-}C_4H_9)_3]_2$. Later, Agaskar and Cotton[18] used data for $Mo_2(O_2CR)_4$ molecules, with the shifts in the free acids, RCO_2H, as reference, and calculated much lower values, viz., $(-2640 \pm 380) \times 10^{-36}$ m^3/molecule. The problem with the latter method of estimation is that the reference may not be entirely valid. In all cases, lack of complete rigidity of the structure may be a source of uncertainty, as may also be the small anisotropies of other structural units besides the M–M bond that are near the test nuclei. In the present work, we believe that the problem of a suitable reference has been eliminated since it was possible to compare the chemical shift difference for two groups that were in identical chemical environments *except* only for their spatial position. We therefore believe that the values obtained in this study are the best available. The χ value of ca. -8800×10^{-36} m^3/molecule is the largest among multiple-bond systems, indicating that the Mo$\overset{4}{-}$Mo bond itself is highly electronically anisotropic.

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Supplementary Material Available: Full listings of bond angles, bond distances, and anisotropic displacement parameters (4 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Structural and Spectroscopic Characterization of the Dirhenium Octakis(isothiocyanato) Salt $(Ph_4As)_2Re_2(NCS)_8 \cdot 2L$ (L = $(CH_3)_2CO$, C_5H_5N). A Unique Case of Axial Coordination in M_2X_8 Compounds

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Molecular structures of two dirhenium(III) octakis(isothiocyanato) compounds, $(Ph_4As)_2Re_2(NCS)_8 \cdot 2(CH_3)_2CO$ (**1**) and $(Ph_4As)_2Re_2(NCS)_8 \cdot 2C_5H_5N$ (**2**), have been established by X-ray crystallography. They were prepared in high yield from $(n\text{-}Bu_4N)_2Re_2Cl_8$ by a ligand-exchange reaction. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with unit cell dimensions a = 14.697 (3) Å, b = 10.949 (3) Å, c = 23.617 (5) Å, β = 99.67 (2)°, V = 3746 (1) $Å^3$, and Z = 2. The $[Re_2(NCS)_8]^{2-}$ anions reside on a crystallographic inversion center and are therefore rigorously eclipsed. The Ph_4As^+ cations reside on a general position. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell dimensions: a = 12.823 (4) Å, b = 13.153 (2) Å, c = 12.762 (3) Å, α = 95.81 (2)°, β = 108.91 (2)°, γ = 118.80 (2)°, V = 1696 (1) $Å^3$, and Z = 1. The $[Re_2(NCS)_8]^{2-}$ anions reside on a crystallographic inversion center, while the Ph_4As^+ cations reside on general positions. Two distinct bands are observed in the electronic spectrum of $Re_2(NCS)_8{}^{2-}$ salts. The band at 990 nm (10.1×10^3 cm^{-1}; ϵ = 3980 M^{-1} cm^{-1}) is assigned to the δ–δ^* transition, while the intense band at 465 nm (ϵ = 21 500 M^{-1} cm^{-1}) is most probably a charge-transfer band from the ligand to the empty metal orbitals.

Introduction

Homoleptic, multiply bonded dimers of the $[M_2X_8]^{n-}$ type have been extensively studied in the past. For X = halogen there are numerous examples of Mo, W, Re, Tc, and Os multiply bonded compounds.[1-3] Very little attention has been paid to M_2X_8 complexes with ligands other than halide ions, viz., SCN^-, OCN^-, N_3^-, etc. Only thiocyanato complexes have received limited at-

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tention so far. The first homoleptic octakis(thiocyanato) dimer was structurally characterized by Bino, Cotton, and Fanwick[4] as $(NH_4)_4Mo_2(NCS)_8{\cdot}xH_2O$ (x = 4, 6). The Mo–Mo bond lengths are 2.162 (1) and 2.177 (1) Å in two independent molecules found in the unit cell and are slightly longer than those in other Mo-Mo quadruple bonds.

Octakis(isothiocyanato)dirhenate, $[Re_2(NCS)_8]^{2-}$, was first reported 20 years ago,[8] but despite numerous attempts, crystals suitable for X-ray diffraction experiments have never heretofore been obtained. Additional compounds with thiocyanato ligands include the following: $Mo_2(NCS)_4(PR_3)_4$,[5] prepared by ligand exchange from $Mo_2Cl_4(PR_3)_4$; $Mo_2(NCS)_4(dppm)_2{\cdot}2(CH_3)_2CO$[6] (in which there is no interaction between $Mo_2(NCS)_4(dppm)_2$ and the acetone molecule), prepared by reacting $Mo_2(MeSO_3)_4$ with dppm in the presence of NH_4SCN; mixed amino acid–thiocyanato complexes,[7] $Mo_2(O_2CCH(NH_3)R)_2(NCS)_4{\cdot}nH_2O$ (R = H, n = 1; R = $CH(CH_3)CH_2CH_3$, n = 4.5), obtained from $K_4Mo_2Cl_8$ in the presence of the amino acid, KSCN, and *p*-toluenesulfonic acid. Preliminary investigation of the chemistry[8,9] of the $[Re_2(NCS)_8]^{2-}$ ion indicated that the Re–Re quadruple bond may be weak, since most of the reactions resulted in its cleavage. This weakening of the metal–metal bond was attributed to the effect of the thiocyanato ligands. In view of these observations it was considered important to obtain the bond distance for the dirhenium octakis(thiocyanato) anion and compare it to that in other rhenium compounds.

We report here that we have successfully grown crystals of two $(Ph_4As)_2Re_2(NCS)_8{\cdot}2L$ (L = $(CH_3)_2CO$, C_5H_5N) compounds and investigated them by single-crystal X-ray diffraction. We have also reexamined the electronic spectra of these complexes and assigned the band at 990 nm to the δ–δ^* transition.

Experimental Section

Starting Materials. Tetra-*n*-butylammonium octachlorodirhenate was prepared according to a literature procedure.[10] Solvents were freshly distilled from appropriate drying agents. All reactions were carried out under an argon atmosphere unless stated otherwise.

Preparation of $(Ph_4As)_2Re_2(NCS)_8$. The preparation of this compound was described before, but the visible spectrum reported suggested that it was not obtained pure.

Tetra-*n*-butylammonium octachlorodirhenate (0.30 g, 0.27 mmol), NaSCN (0.2 g, 2.5 mmol), 0.35 mL of acetic acid, and 20 mL of MeOH were stirred together for 1 h at 25–30 °C. After this time all the reagents had dissolved and the reaction mixture was dark red–orange. A solution of Ph_4AsCl (0.42 g, 1.0 mmol) in 10 mL of MeOH was added dropwise via syringe, causing an orange, crystalline precipitate to be deposited. The reaction mixture was cooled to 0 °C for 1 h and filtered. The solid was washed with methanol and ethyl ether and finally vacuum-dried. The yield was 0.36 g (85%) of orange-red crystalline solid. IR (cm^{-1}, Nujol mull, KBr plate): 2040 vs (C≡N), 1090 w, 1000 w, 745 w, 695 w. IR (cm^{-1}, Nujol mull, CsI plate): 485 w, 470 w. UV–vis (λ, nm (ϵ, M^{-1} cm^{-1}), acetone solution): 987 (3980), 630 (shoulder), 520 (shoulder), 465 (21 500). ^1H NMR (ppm): 7.85 (multiplet).

The purity of the compound was most conveniently checked by monitoring the C≡N stretching region in the IR spectrum. Only one broad band arising from the presence of the terminal ligands should be present. Contamination with $[Re_2(NCS)_{10}]^{3-}$ introduces additional C≡N bands at 1915 and 1880 cm^{-1}.

Crystals of the acetone adduct were grown by slow evaporation in air of a solution of $(Ph_4As)Re_2(NCS)_8$ in acetone–toluene. Over a few days of slow evaporation large, block-shaped crystals were formed. They decomposed when removed from the mother liquor.

Table I. Crystallographic Data for Compounds **1** and **2**

formula	$Re_2As_2S_8O_2N_8C_{62}H_{52}$	$Re_2As_2S_8N_{10}C_{66}H_{50}$
fw	1719.91	1761.96
space group	$P2_1/c$	$P\bar{1}$
systematic absences	$0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$	
a, Å	14.697 (3)	12.823 (4)
b, Å	10.949 (3)	13.153 (2)
c, Å	23.617 (5)	12.762 (3)
α, deg	90.0	95.81 (2)
β, deg	99.67 (2)	108.91 (2)
γ, deg	90.0	118.80 (2)
V, $Å^3$	3746 (1)	1696 (1)
Z	2	1
d_{calcd}, g/cm^3	1.525	1.725
cryst size, mm	0.48 × 0.55 × 0.60	0.1 × 0.3 × 0.3
μ(Mo Kα), cm^{-1}	44.03	48.637
data collecn instrument	$P\bar{1}$	Rigaku AFC5R
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)	
orientation rflcns: no.; range (2θ), deg	15; 20 < 2θ	25; 14.6 < 2θ < 22.2
temp, °C	20	22
scan method	ω	ω–2θ
data collecn range, 2θ, deg	4–50	4–45
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6857, 3839	4467, 3788
no. of params refined	379	397
transmission factors: max, min	1.00, 0.87	1.3862, 0.8001
R^a	0.0457	0.0496
$R_w{}^b$	0.0599	0.0833
quality-of-fit indicator[c]	1.471	1.817
largest shift/esd, final cycle	0.03	0.03
largest peak, e/$Å^3$	1.755	1.43

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Preparation of the Pyridine Adduct. To an acetone solution of $(Ph_4As)_2Re_2(NCS)_8$ (50 mg, 3.1 × 10^{-5} mol) was added pyridine (1 mL). The test tube with the solution was lightly stoppered with a rubber stopper, allowing slow evaporation of the solvents. In a few days a crop of well-formed parallelepipedal crystals was collected. A typical yield was 50 mg (90%). Crystals of the pyridine adduct are stable in air. The C≡N stretch is at 2040 cm^{-1} (Nujol mull).

Preparation of $(Ph_3MeP)_2Re_2(NCS)_8$. This compound could also be prepared in a very pure state and has the advantage of being more soluble than $(Ph_4As)_2Re_2(NCS)_8$. The method of preparation was identical with that used for $(Ph_4As)_2Re_2(NCS)_8$, except that Ph_3MePCl was used as a precipitating agent. The yields were typically 80–90%.

Physical Measurements. Electronic spectra were recorded with a Cary 17D spectrophotometer. IR spectra were recorded with a Perkin-Elmer 785 spectrometer. ^1H NMR spectra were recorded with a Varian XL-200 spectrometer.

X-ray Structure Analysis. A crystal of $(Ph_4As)_2[Re_2(NCS)_8]{\cdot}2(CH_3)_2CO$ (**1**) was mounted inside a thin-walled glass capillary with a drop of mother liquor. The crystal was found to be monoclinic. The presence of a mirror plane as well as the cell dimensions were confirmed by axial photographs. A crystal of $(Ph_4As)_2[Re_2(NCS)_8]{\cdot}2C_5H_5N$ (**2**) was mounted on top of a glass fiber. It was found to be triclinic, and the cell dimensions were confirmed by axial photographs. For **1** data were collected in the range $0 \rightarrow h$, $0 \rightarrow k$, $-l \rightarrow +l$ ad for **2** in the range $0 \rightarrow h$, $-k \rightarrow +k$, $l \rightarrow +l$. Data reduction was carried out by standard procedures,[11] including corrections for Lorentz and polarization effects. Empirical absorption corrections based on six azimuthal scans (ψ scans) of selected reflections with Eulerian χ angle near 90° were applied.[12] Pertinent crystallographic data are summarized in Table I.

Structure Solution and Refinement. $(Ph_4As)_2[Re_2(NCS)_8]{\cdot}2(CH_3)_2CO$ (1). The positions of Re atoms were found from the Patterson function. A subsequent difference Fourier map revealed the position of the As atom. The positions of the remaining non-hydrogen atoms were found by alternating cycles of least-squares refinement and difference Fourier

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Table II. Positional Parameters and Their Estimated Standard Deviations for $(Ph_4As)_2Re_2(NCS)_8\cdot2(CH_3)_2CO$ (**1**) and $(Ph_4As)_2Re_2(NCS)_8\cdot2C_5H_5N$ (**2**)[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Compound **1**									
Re	0.01886 (4)	0.60051 (5)	0.50003 (2)	3.380 (8)	C(21)	0.573 (1)	0.782 (2)	0.1204 (6)	6.0 (4)
As	0.66725 (9)	0.7884 (1)	0.23581 (6)	3.68 (3)	C(22)	0.561 (1)	0.817 (2)	0.0622 (7)	7.6 (5)
S(1)	0.1113 (4)	0.6563 (5)	0.3193 (2)	8.4 (1)	C(23)	0.621 (1)	0.902 (2)	0.0429 (7)	7.9 (5)
S(2)	0.6667 (3)	0.4021 (5)	0.4094 (2)	7.3 (1)	C(24)	0.693 (1)	0.949 (2)	0.0809 (7)	6.9 (5)
S(3)	−0.0674 (3)	0.7514 (4)	0.6714 (2)	5.9 (1)	C(25)	0.705 (1)	0.918 (1)	0.1392 (6)	5.1 (3)
S(4)	−0.2748 (3)	0.7717 (5)	0.4296 (2)	7.3 (1)	C(30)	0.7237 (9)	0.921 (1)	0.2816 (6)	4.7 (3)
N(1)	0.0602 (7)	0.609 (1)	0.4235 (4)	4.1 (2)	C(31)	0.669 (1)	0.993 (1)	0.3124 (6)	5.8 (4)
N(2)	0.8487 (7)	0.412 (1)	0.4623 (4)	4.1 (2)	C(32)	0.711 (1)	1.088 (2)	0.3437 (8)	7.6 (5)
N(3)	−0.0127 (7)	0.6534 (9)	0.5760 (4)	4.1 (2)	C(33)	0.797 (2)	1.113 (2)	0.3440 (7)	9.4 (6)
N(4)	−0.1031 (7)	0.668 (1)	0.4640 (4)	4.2 (2)	C(34)	0.856 (1)	1.047 (2)	0.3152 (8)	9.7 (5)
C(1)	0.0825 (9)	0.628 (1)	0.3811 (6)	4.6 (3)	C(35)	0.816 (1)	0.949 (2)	0.2823 (7)	6.8 (4)
C(2)	0.7731 (8)	0.409 (1)	0.4400 (5)	4.1 (3)	C(40)	0.7454 (8)	0.650 (1)	0.2454 (5)	4.2 (3)
C(3)	−0.0360 (8)	0.694 (1)	0.6174 (5)	3.6 (3)	C(41)	0.7466 (9)	0.572 (1)	0.1987 (6)	4.7 (3)
C(4)	−0.1749 (9)	0.711 (1)	0.4503 (5)	4.1 (3)	C(42)	0.801 (1)	0.467 (1)	0.2057 (7)	5.7 (4)
C(10)	0.5527 (9)	0.754 (1)	0.2612 (6)	4.5 (3)	C(43)	0.859 (1)	0.444 (1)	0.2590 (7)	6.3 (4)
C(11)	0.5535 (9)	0.667 (1)	0.3044 (6)	5.0 (3)	C(44)	0.857 (1)	0.524 (2)	0.3054 (8)	7.1 (5)
C(12)	0.471 (1)	0.645 (2)	0.3253 (7)	6.4 (4)	C(45)	0.799 (1)	0.627 (2)	0.2996 (7)	5.9 (4)
C(13)	0.390 (1)	0.715 (2)	0.3017 (7)	6.3 (4)	O(1)	0.0711 (8)	0.676 (1)	−0.0011 (5)	6.8 (3)
C(14)	0.395 (1)	0.796 (2)	0.2600 (7)	6.2 (4)	C(5)	0.088 (2)	0.597 (2)	−0.0315 (8)	9.4 (6)
C(15)	0.4756 (9)	0.821 (1)	0.2382 (7)	5.3 (4)	C(6)	0.009 (2)	0.586 (2)	−0.090 (1)	12.4 (8)
C(20)	0.6462 (9)	0.839 (1)	0.1570 (5)	3.9 (3)	C(7)	0.133 (2)	0.481 (2)	−0.022 (1)	14.7 (9)
Compound **2**									
Re	0.05981 (4)	0.60248 (4)	0.01145 (4)	2.59 (1)	C(22)	0.695 (2)	0.577 (1)	0.197 (1)	6.4 (5)
As	0.7009 (1)	0.7879 (1)	0.4653 (1)	3.00 (3)	C(23)	0.819 (1)	0.590 (1)	0.251 (1)	6.2 (5)
S(1)	0.9322 (4)	0.3805 (4)	0.3539 (3)	6.0 (1)	C(24)	0.905 (1)	0.659 (1)	0.364 (1)	5.3 (4)
S(2)	0.4811 (3)	0.7120 (4)	0.0537 (4)	5.5 (1)	C(25)	0.872 (1)	0.720 (1)	0.430 (1)	4.3 (4)
S(3)	0.2915 (4)	0.3365 (4)	0.0881 (5)	6.3 (1)	C(30)	0.842 (1)	0.879 (1)	0.618 (1)	3.3 (3)
S(4)	0.2525 (4)	0.8039 (4)	0.4133 (4)	6.4 (1)	C(31)	0.910 (1)	1.007 (1)	0.652 (1)	3.7 (4)
N(1)	0.9615 (9)	0.4046 (8)	0.1524 (8)	3.2 (3)	C(32)	1.014 (1)	1.072 (1)	0.765 (1)	5.0 (4)
N(2)	0.2346 (9)	0.6278 (8)	0.0455 (9)	3.3 (3)	C(33)	1.048 (1)	1.010 (1)	0.835 (1)	5.2 (5)
N(3)	0.0864 (9)	0.3701 (8)	0.0206 (9)	3.3 (3)	C(34)	0.978 (1)	0.884 (1)	0.799 (1)	4.8 (4)
N(4)	0.1196 (9)	0.6644 (8)	0.1824 (9)	3.5 (3)	C(35)	0.877 (1)	0.819 (1)	0.692 (1)	4.4 (4)
N(10)	0.1963 (9)	0.8303 (8)	0.0447 (9)	3.5 (3)	C(50)	0.540 (1)	0.680 (1)	0.475 (1)	3.6 (3)
C(1)	0.951 (1)	0.395 (1)	0.236 (1)	3.3 (3)	C(51)	0.426 (1)	0.608 (1)	0.371 (2)	5.6 (5)
C(2)	0.338 (1)	0.6629 (9)	0.049 (1)	3.0 (3)	C(52)	0.306 (2)	0.540 (1)	0.381 (2)	6.6 (6)
C(3)	0.172 (1)	0.355 (1)	0.049 (1)	3.6 (4)	C(53)	0.303 (1)	0.541 (1)	0.486 (2)	6.3 (5)
C(4)	0.174 (1)	0.722 (1)	0.279 (1)	3.7 (3)	C(54)	0.417 (2)	0.610 (2)	0.589 (2)	7.8 (6)
C(10)	0.184 (1)	0.904 (1)	0.113 (1)	3.7 (3)	C(55)	0.539 (1)	0.679 (2)	0.583 (1)	5.8 (5)
C(11)	0.257 (1)	0.029 (1)	0.137 (1)	4.3 (4)	C(60)	0.672 (1)	0.894 (1)	0.389 (1)	3.4 (3)
C(12)	0.349 (1)	0.080 (1)	0.093 (1)	4.5 (4)	C(61)	0.565 (1)	0.903 (1)	0.375 (1)	3.5 (3)
C(13)	0.359 (1)	0.004 (1)	0.019 (1)	4.0 (4)	C(62)	0.551 (1)	0.986 (1)	0.320 (1)	4.9 (4)
C(14)	0.719 (1)	0.121 (1)	0.002 (1)	3.6 (3)	C(63)	0.640 (1)	1.058 (1)	0.280 (1)	4.8 (4)
C(20)	0.751 (1)	0.707 (1)	0.378 (1)	3.3 (3)	C(64)	0.748 (1)	1.051 (1)	0.294 (1)	4.8 (4)
C(21)	0.661 (1)	0.637 (1)	0.263 (1)	5.4 (5)	C(65)	0.767 (1)	0.967 (1)	0.349 (1)	4.2 (4)

[a] Anisotropically refined atms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

maps. A final difference Fourier map revealed residual electron density around the inversion center. All attempts to model it as a disordered solvent molecule failed, giving large thermal parameters and unreasonable bond distances and angles. Convergence was reached by using 3839 data with $F_o^2 > 3\sigma(F_o^2)$ to fit 379 parameters (data to parameter ratio 10.13). The largest shift/esd in a final cycle was 0.03. The refinement gave residuals of $R = 0.0457$ and $R_w = 0.0599$ and a quality-of-fit indicator of 1.47.

$(Ph_4As)_2[Re_2(NCS)_8]\cdot2C_5H_5N$ (2). The structure was solved by a Patterson interpretation provided by the SHELXS-86 program, which revealed almost the complete $Re_2(NCS)_8$ unit and a large part of the cation. After a few cycles of a least-squares refinement the remaining non-hydrogen atoms were located in a difference Fourier map. At the end of the refinement it became apparent that the structure was troubled by absorption problems, despite the earlier empirical absorption correction. The program DIFABS[13] was applied to the data. All non-hydrogen atoms were refined anisotropically. The final residuals were $R = 0.0496$ and $R_w = 0.0833$. The quality-of-fit indicator was 1.43.

Results and Discussion

Preparation of $[Re_2(NCS)_8]^{2-}$ Salts. Ligand exchange of Cl^- for SCN^- in acidified methanol occurs in high yield. Upon addition of Ph_4AsCl or Ph_3MePCl the appropriate salts precipitate from the reaction mixture, from which they can be easily separated. We have also tried to grow crystals of $(n\text{-}Bu_4N)_2[Re_2(NCS)_8]$, but the only crystals obtained were these of $(n\text{-}Bu_4N)_3[Re_2(NCS)_{10}]$. Their identity[14] was confirmed by IR spectroscopy, which shows the C≡N stretch of the bridging SCN^- group at 1915 and 1880 cm^{-1} in addition to the C≡N stretch of the terminal ligands at 2040 cm^{-1}. A unit cell determination of a selected crystal gave results identical with those described before.[14] This compound could be obtained in high yield by dissolving $(n\text{-}Bu_4N)_2[Re_2(NCS)_8]$ in CH_2Cl_2, adding an excess of $n\text{-}Bu_4NSCN$, and allowing slow evaporation of the solvent. $(n\text{-}Bu_4N)_2[Re_2(NCS)_8]$ is quite soluble in MeOH and difficult to crystallize from the reaction mixture. On the other hand, the cations Ph_4As^+ and Ph_3MeP^+ cause precipitation of crystalline products free from any contaminants. $(Ph_4As)_2[Re_2(NCS)_8]$ is indefinitely stable in air in the solid state and in acetone solution did not decompose to any detectable extent over a period of 1 week, as monitored by UV–vis spectroscopy.

Structural Results. Table II lists the atomic positional parameters and equivalent isotropic thermal displacement parameters for both compounds, and Table III presents the most important

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(13) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(14) Cotton, F. A.; Davison, A.; Ilsley, W. H.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 2719.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $(Ph_4As)_2Re_2(NCS)_8{\cdot}2(CH_3)_2CO$ (**1**) and $(Ph_4As)_2Re_2(NCS)_8{\cdot}2C_5H_5N$ (**2**)[a]

		Compound **1**			
Re–Re	2.270 (1)	Re–O(1)	2.564 (10)	N(1)–C(1)	1.12 (2)
Re–N(1)	2.003 (10)	S(1)–C(1)	1.616 (15)	N(2)–C(2)	1.147 (15)
Re–N(2)	2.005 (9)	S(2)–C(2)	1.611 (12)	N(3)–C(3)	1.18 (2)
Re–N(3)	2.013 (11)	S(3)–C(3)	1.560 (13)	N(4)–C(4)	1.15 (2)
Re–N(4)	1.994 (10)	S(4)–C(4)	1.609 (13)		
Re–Re–N(1)	98.9 (3)	N(1)–Re–O(1)	79.1 (4)	Re–N(2)–C(2)	174 (1)
Re–Re–N(2)	98.7 (3)	N(2)–Re–N(3)	88.6 (4)	Re–N(3)–C(3)	173 (1)
Re–Re–N(3)	100.7 (3)	N(2)–Re–N(4)	162.1 (4)	Re–N(4)–C(4)	171 (1)
Re–Re–N(4)	99.2 (3)	N(2)–Re–O(1)	78.5 (4)	S(1)–C(1)–N(1)	178 (1)
Re–Re–O(1)	176.6 (3)	N(3)–Re–N(4)	87.0 (4)	S(2)–C(2)–N(2)	179 (1)
N(1)–Re–N(2)	89.2 (4)	N(3)–Re–O(1)	81.3 (4)	S(3)–C(3)–N(3)	179 (1)
N(1)–Re–N(3)	160.4 (4)	N(4)–Re–O(1)	83.6 (4)	S(4)–C(4)–N(4)	179 (1)
N(1)–Re–N(4)	89.2 (4)	Re–N(1)–C(1)	172 (1)		
		Compound **2**			
Re–Re	2.296 (1)	S(2)–C(2)	1.603 (15)	N(10)–C(10)	1.34 (2)
Re–N(1)	2.005 (11)	S(3)–C(3)	1.60 (2)	N(10)–C(14)	1.32 (2)
Re–N(2)	1.986 (12)	S(4)–C(4)	1.604 (13)	C(10)–C(11)	1.38 (2)
Re–N(3)	2.000 (13)	N(1)–C(1)	1.13 (2)	C(11)–C(12)	1.39 (2)
Re–N(4)	1.992 (10)	N(2)–C(2)	1.16 (2)	C(12)–C(13)	1.39 (3)
Re–N(10)	2.536 (9)	N(3)–C(3)	1.16 (2)	C(13)–C(14)	1.39 (2)
S(1)–C(1)	1.62 (2)	N(4)–C(4)	1.15 (2)		
Re–Re–N(1)	99.8 (3)	N(2)–Re–N(10)	79.9 (4)	S(1)–C(1)–N(1)	178 (1)
Re–Re–N(2)	99.5 (3)	N(3)–Re–N(4)	90.7 (5)	S(2)–C(2)–N(2)	180 (2)
Re–Re–N(3)	97.9 (3)	N(3)–Re–N(10)	82.9 (4)	S(3)–C(3)–N(3)	179 (1)
Re–Re–N(4)	98.0 (3)	N(4)–Re–N(10)	80.0 (4)	S(4)–C(4)–N(4)	179 (1)
Re–Re–N(10)	177.9 (2)	Re–N(1)–C(1)	168.4 (8)	N(10)–C(10)–C(11)	122 (2)
N(1)–Re–N(2)	86.8 (5)	Re–N(2)–C(2)	162 (1)	C(10)–C(11)–C(12)	119 (2)
N(1)–Re–N(3)	89.1 (5)	Re–N(3)–C(3)	174 (1)	C(11)–C(12)–C(13)	119 (1)
N(1)–Re–N(4)	162.1 (4)	Re–N(4)–C(4)	166 (1)	C(12)–C(13)–C(14)	118 (2)
N(1)–Re–N(10)	82.2 (4)	Re–N(10)–C(10)	118.5 (9)	N(10)–C(14)–C(13)	123 (2)
N(2)–Re–N(3)	162.6 (4)	Re–N(10)–C(14)	122 (1)		
N(2)–Re–N(4)	88.1 (5)	C(10)–N(10)–C(14)	119 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

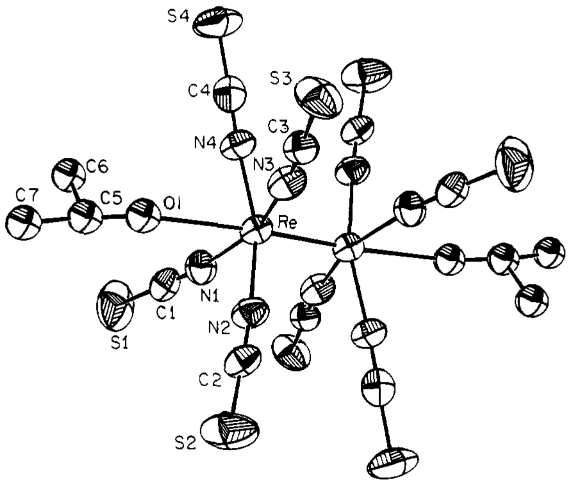

Figure 1. ORTEP diagram of the $Re_2(NCS)_8{\cdot}2(CH_3)_2CO$ anion drawn at the 50% probability level. Atoms of the acetone molecule have been assigned arbitrary thermal parameters for the sake of clarity. The unlabeled part of the molecule is related by the inversion center.

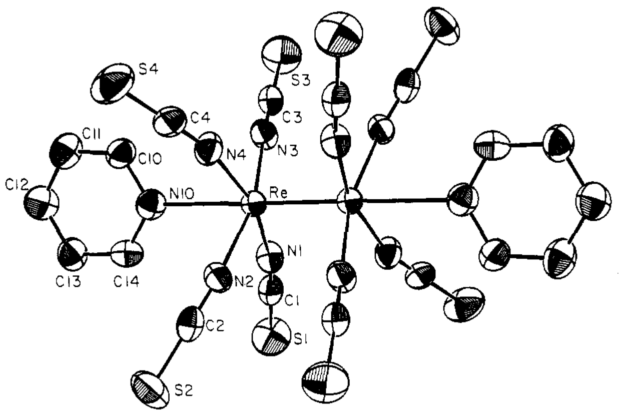

Figure 2. ORTEP view of the $Re_2(NCS)_8{\cdot}2C_5H_5N$ anion drawn at the 50% probability level. The unlabeled part of the molecule is related by the inversion center.

interatomic distances and angles in the $[Re_2(NCS)_8L_2]^{2-}$ ions. Figures 1 and 2 show the structures of the two anions. The cations, which in each case reside on general positions, were refined well and show no unusual features. The packing contacts all appear to be normal. Drawings of the unit cells are available as supplementary material.

In each compound the anion resides on an inversion center and is thus constrained to have an eclipsed rotational conformation. The thiocyanate ligands are, as in the previously studied dimolybdenum species, N-bonded (i.e., strictly speaking, they should be designated as isothiocyanato groups). The NCS ligands themselves are all essentially linear (angles of 178–179°). Somewhat greater deviations from linearity occur in the Re–N–C chains, with these angles ranging 171–174° in **1** and 162–174° in **2**. We attribute these variations to nonbonded contacts and consider that the Re–N–C–S chains are ideally linear but subject to packing distortions. The Re–N distances are all within the narrow range of 1.99 (1)–2.01 (1) Å, meaning that within experimental uncertainty they are all equal at 2.00 ± 0.01 Å. The Re′–Re–N angles are all in the range 97.9 (3)–100.7 (3)°. These are somewhat smaller than those observed in the $[Re_2X_8]^{2-}$ ions, where X = Cl and Br, and probably reflects the smaller size of the N atoms.

We turn now to the interrelated questions of the Re–Re distances and the Re–L distances. The Re–Re distances found here, 2.270 (1) and 2.296 (1) Å for **1** and **2**, respectively, are the longest ones so far found for $[Re_2X_8]^{2-}$ ions. All others,[15a] for X = Cl, Br, and CH_3, are in the range 2.178 (1)–2.252 (2) Å. At the same time, these are the only two $[Re_2X_8]^{2-}$ species that have been found

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(15) See ref 1: (a) p 41; (b) p 344; (c) p 405.

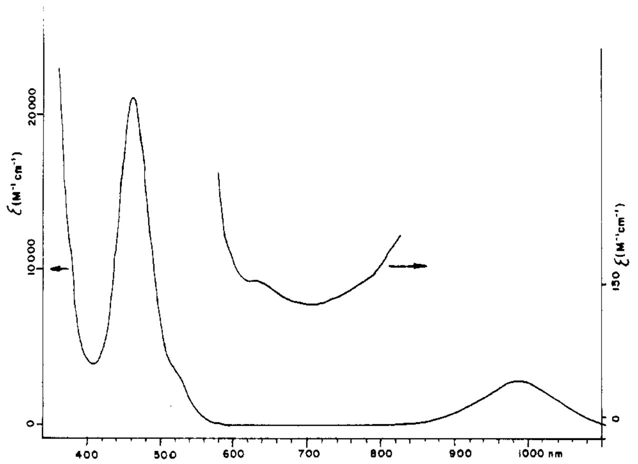

Figure 3. Electronic spectrum of $(Ph_4As)_2Re_2(SCN)_8{\cdot}2(CH_3)_2CO$ in acetone.

to contain axial ligands, except for the $[Re_2Cl_8(H_2O)_2]^{2-}$ ion in $Cs_2Re_2Cl_8{\cdot}H_2O$.[16] Interestingly, in that compound, which contains both $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_8(H_2O)_2]^{2-}$ ions, the latter has an Re–Re distance of 2.252 (2) Å while the former has an Re–Re distance of only 2.237 (2) Å. The axial water interaction would appear to be rather weak (Re–O = 2.66 Å), but it is nevertheless sufficient to cause an increase of 0.015 (3) Å in the Re–Re distance. With the stronger axial coordination in the present compounds (Re–O = 2.56 (1) Å and Re–N = 2.54 (1) Å), it is possible that the long Re–Re distances might be said to signify nothing more than that the usual inverse relationship between M–M and $M-L_{ax}$ distances is operating here. Since we have not obtained any crystalline compound in which the $[Re_2(NCS)_8]^{2-}$ ion is not axially ligated, we cannot say whether the thiocyanate ligand itself has the effect of lengthening the Re–Re bond. One of the most interesting things about these crystal structures is something that does *not* happen—namely, there is *no* disorder of the Re_2 units such that some of them lie in a direction perpendicular to the direction of the majority. In all cases of $[M_2X_8]^{n-}$ ions with X = Cl and Br, in which there is an eclipsed rotational geometry, this kind of disorder is found,[15b] varying from as little as 7% to as m uch as 35%. A little reflection will show, however, that this is exactly what should be expected. In M_2X_8 units with X = Cl and Br, the X_8 set is practically cubic. This means that one M_2X_8 unit can lie perpendicular to its neighbors without encountering serious packing problems. The $[Re_2(NCS)_8]^{2-}$ ion, because of the rodlike shape of the ligands (abetted by the unusually small Re′–Re–N angles) is nowhere nearly cubic in outside dimensions. It is a square parallelepiped with a short fourfold axis (a wafer). As such, its orientation within the crystal environment cannot be changed by 90° as for the M_2Cl_8 or M_2Br_8 species.

Electronic Spectrum. Our study of the electronic spectrum of $(Ph_4As)_2[Re_2(NCS)_8]$ in acetone solution shows (Figure 3) that there are only two major bands. Previous results[8] were somewhat confusing, solutions in acetonitrile apparently suffering from decomposition, although those results obtained by diffuse reflection from solids appear to be correct. In addition to the two major bands there are several weak features, as is also the case for $[Re_2Cl_8]^{2-}$, attributable to forbidden transitions.[15c] One major band is at 987 nm (10.13×10^5 cm^{-1}) with a molar extinction of 3980 M^{-1} cm^{-1}. This band can be assigned to the $\delta \rightarrow \delta^*$ singlet transition, and it is the lowest energy ever observed for such a transition in a quadruply bonded dimetal system. By comparison with other cases, the corresponding singlet–triplet transition could be below 4000 cm^{-1}. Further studies of these transitions in $[Re_2(NCS)_8]^{2-}$ would be of interest.

The $\delta \rightarrow \delta^*$ transition energy shows solvent dependence since, as the crystal structures show, $[Re_2(NCS)_8]^{2-}$ is prone to have axial ligation. The band positions for several solvents are as follows: CH_2Cl_2, 980 nm; acetone, 987 nm; dimethyl sulfoxide, 1012 nm; pyridine, 1025 nm. These changes presumably correspond to the lengthening of the Re–Re bond with increasingly strong axial ligation.

The other major band is at 465 nm (21.5×10^3 cm^{-1}) and has a molar extinction coefficient of 21 500 M^{-1} cm^{-1}. This very intense band is undoubtedly a charge-transfer band, and it accounts for the yellow color of the $[Re_2(NCS)_8]^{2-}$ ion.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Full listings of bond distances, bond angles, and anisotropic-equivalent displacement parameters and cell packing diagrams for **1** and **2** (10 pages); tables of observed and calculated structure factors for both compounds (39 pages). Ordering information is given on any current masthead page.

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[16] Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1977**, *16*, 1867.