denominator of the expression on the right-hand side of the equation.

In Table II we have compared the experimental values of $\Delta G_x°$ with the values obtained by our model (eq 23). In pure KNO_3 melt the bond-energy parameter ΔE_1 for $Z_2 = 6$ is -20.0 kJ mol^{3-1}, and for $Z_2 = 4$ it is -22.0 kJ mol^{-1}. (Since $\Delta G_1°$ is obtained experimentally, the value of ΔE_1 depends on the coordination number Z_2 adopted. This is also true for ΔE_2 (eq 11 and 7).) Since direct measurements in pure $Ca(NO_3)_2$ were not feasible, we use a value of ΔE_2 based on measurements in $Ca(NO_3)_2$–$x$$H_2O$ melts, extrapolated to $x = 0$ (i.e., to anhydrous melt).[3] This value is -18.8 ± 0.8 kJ mol^{-1} for $Z_2 = 6$, and we have tested several values between -18.0 and -19.6 kJ mol^{-1}. Since higher values gave somewhat better fits, we adopted the value -18.0 kJ mol^{-1} for $Z_2 = 6$. The model was tested with $Z_2 = 6$ and 4 and $Z_1 = 6$ and 4. For the sake of comparison, in Table II are also listed the data obtained by Flood's equation (eq 13) and by the model of Bombi and Sacchetto.[6] The last model refers to charge-symmetrical melts, but it could be applied to the present system under the assumptions that $Ca(NO_3)_2$ in the melt behaves as a 1:1 salt, i.e., as $Ca(NO_3)^+ + NO_3^-$, and $Z_2 = Z_1 = Z$. According to that model

$$\Delta G_x° = RT \ln [x \exp(\Delta E_1/RT) + (1 - x) \exp(\Delta E_2/RT)] - RT \ln Z \quad (24)$$

As seen from Table II, the values obtained by the three models are rather close, and the ratio φ of eq 23 has, indeed, only a slight influence. The $\Delta G_x°$ values in Table II differ relatively little. This is partly due to the narrow energy range between ΔE_1 and ΔE_2, so that $\Delta G_x°$ varies slightly with composition, and partly to the fact that an increase of T decreases K_1; hence $\Delta G_x°$ varies only moderately with temperature.

The models reproduce the experimental $\Delta G_x°$ values fairly well if we take into account the uncertainty of the ΔE_2 parameter and the standard deviations of the experimental values (which are 0.1–0.5 kJ mol^{-1}). However, the present system does not allow us to test and compare more precisely the models, since the data are spread in a too narrow energy range: ΔE_1 and ΔE_2 differ only by 2 kJ mol^{-1}. For a precise evaluation of the models more data on systems covering a wider energy range are required, possibly with a difference $|\Delta E_1 - \Delta E_2|$ of at least 4 kJ mol^{-1}.

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Registry No. $CdCl_2$, 10108-64-2; $CdCl^+$, 14457-58-0; KNO_3, 7757-79-1; $Ca(NO_3)_2$, 10124-37-5.

Supplementary Material Available: A linear regression analysis of emf data (see eq 1–3) and tables of emf measurements (3 pages). Ordering information is given on any current masthead page.

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Mixed Amino Acid–Thiocyanato Complexes of Dimolybdenum(II)

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When solutions of $Mo_2(O_2CCH(NH_3)R)_4^{4+}$ and KNCS are mixed, red to red-purple crystalline compounds of composition $Mo_2(O_2CCH(NH_3)R)_2(NCS)_4 \cdot nH_2O$ can be obtained. Two of these, the glycinate (R = H, $n = 1$; **1**) and the L-isoleucinate ($R = CH(CH_3)CH_2CH_3$, $n = 4.5$; **2**), have been investigated in detail by X-ray crystallography. In each one the molecules have a cisoid arrangement of the amino acid groups and the four N-bonded NCS^- ions together with the molybdenum atoms form a sawhorse arrangement. The Mo–Mo distances range from 2.132 (2) to 2.154 (5) Å in the four crystallographically independent molecules. The crystallographic data are as follows. For **1**: space group $P2_1/n$, $a = 20.877$ (7) Å, $b = 8.928$ (3) Å, $c = 24.346$ (6) Å, $\beta = 105.23$ (5)°, $V = 4379$ (2) Å^3, $Z = 8$. For **2**: space group $P2_1$, $a = 9.034$ (3) Å, $b = 23.807$ (6) Å, $c = 14.489$ (3) Å, $\beta = 93.75$ (5)°, $V = 3109$ (2) Å^3, $Z = 4$.

Introduction

It is well-known that carboxylic acid anions, RCO_2^-, have a strong affinity for the quadruply bonded dimolybdenum moiety, Mo_2^{4+}, as well as other such dimetal units such as Cr_2^{4+}, Tc_2^{6+}, and Re_2^{6+}. One class of carboxylic acids of special importance is amino acids, $RHC(NH_3^+)CO_2^-$; these have been shown to bind strongly to Mo_2^{4+} in aqueous solution,[1] and one compound, $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$, has been isolated and its structure determined X-ray crystallographically. This compound has a structure well adapted to single-crystal polarized spectral studies, and these too have been reported.[2]

Further studies of the complexation of amino acids and peptides by the Mo_2^{4+} moiety have been conducted, and we present here the first of several reports on these investigations.

Table I. Crystallographic Data

	glycinate, **1**	L-isoleucinate, **2**
space group	$P2_1/n$	$P2_1$
a, Å	20.877 (7)	9.034 (3)
b, Å	8.928 (3)	23.807 (6)
c, Å	24.346 (6)	14.489 (3)
β, deg	105.23 (5)	93.75 (5)
V, Å^3	4379 (2)	3109 (2)
d, g/cm$_3$	1.80	1.57
Z	8	4
cryst size, mm	0.08 × 0.1 × 0.1	0.1 × 0.1 ×0.07
μ, cm^{-1}	15.17	10.92
no. of unique data	4333	2866
data with $F_o^2 > n\sigma(F_o^2)$	2902 (n = 3)	1827 (n = 2)
R_1(anisotropic)	0.073	0.080
R_2(anisotropic)	0.101	0.080
esd	1.92	1.24

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(gly)_2(NCS)_4 \cdot H_2O$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.27257 (9)	0.6457 (2)	0.17840 (8)	2.95 (7)	2.51 (8)	3.03 (7)	0.04 (8)	0.76 (6)	0.07 (8)
Mo(2)	0.18579 (10)	0.3657 (2)	−0.19995 (8)	3.52 (8)	2.84 (9)	3.40 (8)	−0.07 (8)	0.67 (7)	−0.26 (8)
Mo(3)	0.16748 (10)	0.3355 (3)	−0.11846 (8)	4.57 (9)	3.9 (1)	3.35 (8)	−0.42 (9)	0.93 (7)	−0.09 (9)
Mo(4)	0.25275 (10)	0.6901 (2)	0.08947 (8)	4.07 (8)	3.30 (9)	2.82 (8)	−0.07 (8)	1.02 (6)	−0.27 (8)
S(1)	0.2995 (3)	0.6346 (7)	0.3075 (3)	5.5 (3)	2.5 (3)	4.3 (3)	1.1 (3)	0.7 (2)	0.4 (2)
S(2)	0.2860 (4)	0.8620 (8)	−0.1835 (3)	8.6 (4)	4.1 (3)	5.4 (3)	−1.8 (3)	3.0 (3)	−0.4 (3)
S(3)	0.4804 (3)	0.3691 (8)	0.2252 (4)	3.0 (3)	4.5 (3)	9.6 (5)	−0.0 (3)	0.4 (3)	0.7 (4)
S(4)	0.2208 (4)	0.8278 (8)	−0.0335 (3)	8.7 (4)	4.3 (3)	4.3 (3)	0.2 (4)	1.2 (3)	−0.6 (3)
S(5)	0.0062 (4)	0.3540 (10)	0.3050 (5)	4.5 (4)	5.8 (4)	14.9 (7)	0.7 (4)	−2.5 (4)	−3.1 (5)
S(6)	0.0518 (4)	0.4563 (13)	0.1378 (13)	4.8 (4)	14.5 (7)	12.0 (6)	1.9 (5)	−0.5 (4)	−6.9 (5)
S(7)	0.1523 (6)	1.2254 (9)	0.0041 (4)	17.0 (7)	5.2 (4)	5.4 (4)	−4.2 (5)	1.9 (5)	−1.4 (3)
O(1)	0.1827 (6)	0.750 (2)	0.1816 (6)	2.5 (6)	2.9 (7)	2.9 (6)	−0.1 (5)	−0.0 (5)	0.3 (5)
O(2)	0.1640 (7)	0.796 (2)	0.0902 (6)	4.8 (7)	5.8 (9)	2.2 (6)	−0.4 (7)	0.9 (5)	−0.4 (6)
O(3)	0.2999 (7)	0.900 (2)	0.1053 (6)	4.8 (7)	4.5 (8)	3.1 (6)	−1.3 (6)	1.5 (5)	−0.0 (6)
O(4)	0.3200 (6)	0.851 (2)	0.1978 (5)	3.6 (6)	3.0 (7)	3.2 (6)	−1.2 (6)	0.3 (5)	0.2 (6)
O(5)	0.1499 (6)	0.147 (2)	−0.2238 (6)	3.3 (6)	3.9 (7)	4.1 (7)	−0.9 (6)	0.8 (5)	−1.2 (6)
O(6)	0.1314 (8)	0.117 (2)	−0.1410 (7)	5.4 (8)	4.7 (9)	5.1 (8)	−0.9 (7)	1.4 (6)	0.1 (7)
O(7)	0.2635 (8)	1.245 (2)	−0.0859 (7)	5.9 (9)	4.1 (8)	4.0 (8)	−0.5 (7)	−1.7 (7)	0.6 (7)
O(8)	0.2827 (7)	0.275 (2)	−0.1710 (6)	5.4 (8)	3.7 (8)	3.7 (7)	0.5 (7)	0.7 (6)	0.0 (6)
N(1)	0.3655 (8)	0.536 (2)	0.1963 (7)	3.5 (8)	4 (1)	3.9 (8)	0.3 (8)	1.0 (7)	0.4 (8)
N(3)	0.2018 (10)	0.496 (2)	0.0565 (8)	7 (1)	4 (1)	3.5 (9)	−1.2 (9)	0.7 (8)	−0.5 (8)
N(4)	0.3356 (10)	0.615 (3)	0.0709 (9)	6 (1)	10 (2)	6 (1)	4 (1)	2.9 (7)	−1 (1)
N(6)	0.2293 (8)	0.438 (2)	0.1817 (7)	4.0 (8)	1.9 (8)	3.3 (8)	0.0 (7)	0.7 (6)	−0.1 (7)
N(7)	0.0971 (8)	0.466 (2)	−0.2487 (7)	3.8 (8)	3.7 (9)	3.9 (9)	0.3 (8)	0.3 (7)	0.2 (8)
N(8)	0.1990 (9)	0.543 (2)	−0.0805 (7)	6 (1)	6 (1)	2.9 (8)	−1 (1)	1.1 (7)	0.3 (9)
N(9)	0.0702 (8)	0.415 (2)	−0.1312 (8)	2.7 (8)	5 (1)	5.0 (9)	0.4 (8)	0.6 (7)	0.1 (9)
N(10)	0.2306 (8)	0.583 (2)	−0.1919 (7)	4.2 (8)	3.4 (9)	3.2 (8)	−0.7 (7)	1.0 (6)	1.0 (7)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
S(8)	0.4440 (8)	0.497 (2)	0.0362 (7)	16.9 (5)	C(5)	0.3228 (10)	0.934 (3)	0.1568 (9)	3.6 (5)
O(56)	0.318 (1)	1.140 (3)	0.038 (1)	12.2 (8)	C(6)	0.1435 (10)	0.582 (3)	0.3292 (9)	3.6 (5)
O(57)	0.409 (2)	0.522 (5)	−0.142 (2)	18.3 (13)	C(7)	0.3690 (14)	1.167 (4)	−0.1015 (13)	7.3 (8)
					C(8)	0.2161 (9)	0.315 (2)	0.1849 (8)	2.9 (4)
N(2)	0.4314 (12)	0.493 (3)	0.4119 (10)	7.8 (6)	C(9)	0.0531 (11)	0.537 (3)	−0.2742 (10)	4.5 (5)
N(5)	0.1203 (9)	0.604 (2)	0.2670 (8)	4.4 (4)	C(10)	0.1333 (10)	0.073 (3)	−0.1889 (9)	3.6 (5)
N(11)	0.1170 (12)	0.879 (3)	−0.2614 (10)	7.4 (6)	C(11)	0.1110 (13)	0.905 (3)	−0.2052 (11)	5.5 (6)
N(12)	0.3840 (22)	1.169 (6)	−0.0438 (20)	18.2 (16)	C(12)	0.2075 (11)	0.663 (3)	−0.0613 (10)	4.6 (5)
C(1)	0.4127 (10)	0.466 (2)	0.2073 (8)	3.1 (4)	C(13)	0.0245 (13)	0.470 (3)	−0.1344 (11)	6.1 (7)
C(2)	0.1489 (10)	0.801 (3)	0.1337 (9)	3.7 (5)	C(14)	0.3008 (12)	1.231 (3)	−0.1219 (11)	5.1 (6)
C(3)	0.4171 (12)	0.377 (3)	0.3635 (10)	4.8 (6)	C(15)	0.2555 (10)	0.696 (3)	−0.1882 (9)	3.5 (5)
C(4)	0.1828 (12)	0.385 (3)	0.0348 (10)	5.0 (6)	C(16)	0.3665 (16)	0.566 (4)	0.0563 (13)	8.1 (9)

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

We describe here two compounds that contain both amino acid ligands and thiocyanate ions. Compounds of this stoichiometry, $(RHC(NH_3)CO_2)_2Mo_2(NCS)_4$, appear to form very readily with any amino acid, and we have selected the glycine (R = H) and L-isoleucine (R = EtMeHC) compounds for detailed structural study.

Experimental Section

Preparations. ***cis*-(glycine)$_2$(NCS)$_4$Mo$_2$ (1).** $K_4Mo_2Cl_8$ (0.1 g), prepared by a literature method,[3] was dissolved in a solution of glycine (2.0 g) and *p*-toluenesulfonic acid (1 g) in 50 mL of H_2O under nitrogen. This solution was allowed to mix by diffusion through a glass frit with a 3 M solution of KNCS at ca. 20 °C. The yellow solution of $Mo_2(gly)_4^{4+}$ slowly turned red, and red crystals were formed over a period of 15 h. The crystals were harvested by filtration, rinsed with water, and dried under vacuum. About 15 mg of crystals was obtained.

***cis*-(L-isoleucine)$_2$(NCS)$_4$Mo$_2$ (2).** The procedure was similar to that just described for the glycine complex. The solution of L-leucine was a saturated solution of the amino acid in 0.2 M hydrochloric acid. The color of the crystalline product is red-purple.

X-ray Crystallography. Data were collected for both compounds on a Syntex $P\bar{1}$ automated four-circle diffractometer by using Mo (λ 0.71073 Å) radiation with a graphite crystal monochromator in the incident beam. A modified version of the Syntex θ–2θ data collection program devised by Dr. P. E. Fanwick was used. Only if the counts during a fast prescan exceeded a predetermined limit were data collected for a reflection. Therefore, weak peaks were not collected, and no output was made to the tape file for further processing.

Rotation photographs and ω scans of several strong reflections indicated in each case that the crystals were of satisfactory quality. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range 25° < 2θ < 45°. Data were collected at 22 ± 3 °C by using the θ–2θ scan technique with a variable scan rate from 4.0 to 24.0°/min. General procedures for data collection

Table III. Bond Distances (Å) and Bond Angles (deg) for $Mo_2(gly)_2(NCS)_4 \cdot H_2O$

Bond Distances for Molecule I			
Mo(1)–Mo(4)	2.132 (2)		
–O(1)	2.11 (1)	Mo(4)–O(2)	2.08 (1)
–O(4)	2.08 (1)	–O(3)	2.11 (1)
–N(1)	2.12 (1)	–N(3)	2.08 (2)
–N(6)	2.07 (1)	–N(4)	2.02 (2)
N(1)–C(1)	1.13 (2)	N(3)–C(4)	1.15 (2)
C(1)–S(3)	1.62 (2)	C(4)–S(7)	1.65 (2)
N(6)–C(8)	1.14 (2)	N(4)–C(16)	1.12 (4)
C(8)–S(1)	1.67 (2)	C(16)–S(8)	1.71 (4)
O(1)–C(2)	1.27 (2)	O(4)–C(5)	1.25 (2)
O(2)–C(2)	1.18 (2)	O(3)–C(5)	1.26 (2)
C(2)–C(3)	1.56 (2)	C(5)–C(6)	1.49 (2)
C(3)–N(2)	1.53 (2)	C(6)–N(5)	1.48 (2)
Bond Distances for Molecule II			
Mo(2)–Mo(3)	2.134 (2)		
–O(5)	2.11 (1)	Mo(3)–O(6)	2.11 (1)
–O(8)	2.12 (1)	–O(7)	2.11 (1)
–N(7)	2.12 (1)	–N(8)	2.10 (2)
–N(10)	2.14 (1)	–N(9)	2.10 (1)
N(7)–C(9)	1.15 (2)	N(8)–C(12)	1.17 (3)
C(9)–S(5)	1.60 (2)	C(12)–S(4)	1.61 (2)
N(10)–C(15)	1.13 (3)	N(9)–C(13)	1.06 (3)
C(15)–S(2)	1.60 (3)	C(13)–S(6)	1.70 (2)
O(5)–C(10)	1.20 (2)	O(8)–C(14)	1.22 (2)
O(6)–C(10)	1.24 (2)	O(7)–C(14)	1.32 (2)
C(10)–C(11)	1.59 (3)	C(14)–C(7)	1.49 (2)
C(11)–N(11)	1.42 (3)	C(7)–N(12)	1.35 (3)
Bond Angles for Molecule I			
Mo(4)–Mo(1)–O(1)	91.0 (3)	Mo(1)–Mo(4)–O(2)	90.6 (3)
–O(4)	91.2 (3)	–O(3)	91.3 (3)
–N(1)	102.6 (4)	–N(3)	100.4 (4)
–N(6)	103.6 (4)	–N(4)	102.5 (5)
O(1)–Mo(1)–O(4)	88.6 (4)	O(2)–Mo(4)–O(3)	88.2 (5)
–N(1)	166.4 (5)	–N(3)	90.8 (6)
–N(6)	89.6 (4)	–N(4)	166.1 (6)
O(4)–Mo(1)–N(1)	90.4 (5)	O(3)–Mo(4)–N(3)	168.2 (5)
–N(6)	165.1 (5)	–N(4)	87.2 (7)
N(1)–Mo(1)–N(6)	87.8 (5)	N(3)–Mo(4)–N(4)	91.0 (8)
S(3)–C(1)–N(1)	178 (1)	S(7)–C(4)–N(3)	177 (2)
S(1)–C(8)–N(6)	177 (2)	S(8)–C(16)–N(4)	167 (4)
Mo(1)–O(1)–C(2)	114 (1)	Mo(1)–O(4)–C(5)	117 (1)
Mo(4)–O(2)–C(2)	118 (1)	Mo(4)–O(3)–C(5)	116 (1)
O(1)–C(2)–O(2)	126 (2)	O(3)–C(5)–O(4)	125 (2)
O(1)–C(2)–C(3)	114 (2)	O(3)–C(5)–C(6)	118 (2)
O(2)–C(2)–C(3)	120 (2)	O(4)–C(5)–C(6)	117 (2)
C(2)–C(3)–N(2)	105 (2)	C(5)–C(6)–N(5)	111 (1)
Bond Angles for Molecule II			
Mo(3)–Mo(2)–O(5)	90.1 (3)	Mo(2)–Mo(3)–O(6)	90.8 (4)
–O(8)	91.8 (3)	–O(7)	90.8 (4)
–N(7)	103.3 (4)	–N(8)	100.8 (4)
–N(10)	102.1 (4)	–N(9)	102.9 (4)
O(5)–Mo(2)–O(8)	88.6 (4)	O(6)–Mo(3)–O(7)	89.0 (5)
–N(7)	92.5 (5)	–N(8)	168.5 (5)
–N(10)	167.4 (5)	–N(9)	90.6 (5)
O(8)–Mo(2)–N(7)	164.8 (5)	O(7)–Mo(3)–N(8)	90.9 (5)
–N(10)	87.8 (5)	–N(9)	166.4 (6)
N(7)–Mo(2)–N(10)	87.9 (5)	N(8)–Mo(3)–N(9)	86.8 (6)
S(5)–C(9)–N(7)	175 (2)	S(4)–C(12)–N(8)	179 (1)
S(2)–C(15)–N(10)	176 (3)	S(6)–C(13)–N(9)	175 (2)
Mo(2)–O(5)–C(10)	118 (1)	Mo(2)–O(8)–C(14)	118 (1)
Mo(3)–O(6)–C(10)	116 (1)	Mo(3)–O(7)–C(14)	117 (1)
O(5)–C(10)–O(6)	125 (2)	O(8)–C(14)–O(7)	122 (2)
–C(11)	118 (2)	–C(7)	118 (2)
O(6)–C(10)–C(11)	117 (2)	O(7)–C(14)–C(7)	119 (1)
C(10)–C(11)–N(11)	108 (2)	C(14)–C(7)–N(12)	106 (2)

have been reported elsewhere.[4] Crystallographic data and other pertinent information are given in Table I. For each crystal, Lorentz and polarization corrections were applied. No absorption correction was applied.

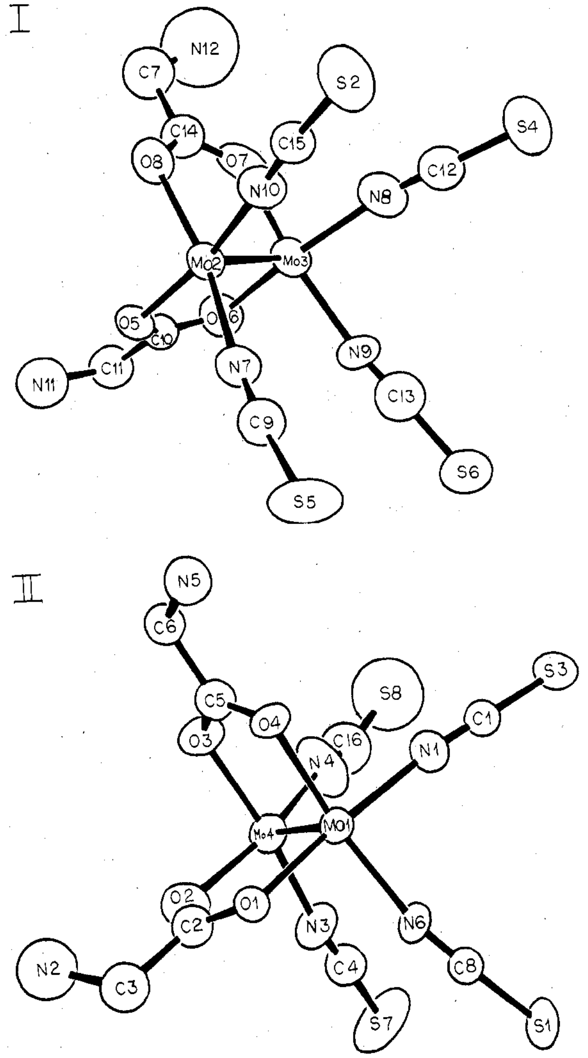

Figure 1. ORTEP projections of the two independent molecules in $Mo_2(gly)_2(NCS)_4 \cdot H_2O$ showing the atomic numbering used in Tables II and III.

Solution and Refinement of the Structures.[5] The heavy-atom positions were obtained in each case by direct methods by using the MULTAN program. The structure of **1** was refined in space group $P2_1/n$ to convergence with anisotropic thermal parameters for the Mo and S atoms and for all the coordinated oxygen and nitrogen atoms. The structure of **2** was refined in space group $P2_1$ to convergence with anisotropic thermal parameters only for the Mo atoms.

The final discrepancy indices defined as

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

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

are listed in Table I. The final difference maps showed no peaks of structural significance.

Results and Discussion

$Mo_2(gly)_2(NCS)_4 \cdot H_2O$. With eight molecules in the unit cell of space group $P2_1/n$ there are two molecules in the asymmetric unit, and no crystallographic symmetry is imposed upon either one. The two molecules are depicted in Figure 1, where the atomic numbering scheme is defined. Table II lists the atomic positional and thermal parameters, and Table III gives the interatomic distances and angles.

The two molecules are essentially identical. Distances and angles within the ligands are all normal. The thiocyanate ions are coordinated through the nitrogen atoms and are essentially linear. The coordination geometry around each metal atom is distorted from square in the sense that the nitrogen atoms are out of the O–Mo–O planes. The Mo–Mo′–O angles are

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for Mo_2(L-isoleu)$_2$(NCS)$_4$·4.5H_2O[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	−0.1534 (4)	−0.3359 (0)	−0.8693 (2)	2.7 (2)	2.9 (2)	2.1 (1)	0.0 (2)	0.8 (1)	0.2 (2)
Mo(2)	−0.3822 (4)	−0.3457 (2)	−0.3836 (2)	2.9 (2)	3.5 (2)	1.8 (1)	0.4 (2)	0.6 (1)	0.1 (2)
Mo(3)	−0.1329 (4)	−0.3819 (2)	−0.9959 (2)	2.8 (2)	2.8 (2)	1.7 (1)	−0.1 (2)	0.1 (1)	0.4 (2)
Mo(4)	−0.3756 (4)	−0.3948 (2)	−0.5074 (2)	2.5 (2)	3.5 (2)	1.9 (1)	−0.3 (2)	0.3 (1)	0.0 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
S(1)	−0.458 (1)	−0.2776 (5)	−1.2161 (7)	3.2 (2)	C(1)	−0.353 (4)	−0.420 (1)	−0.752 (2)	1.4 (8)
S(2)	−0.406 (1)	−0.4699 (5)	−0.6835 (7)	3.0 (2)	C(2)	−0.349 (4)	−0.487 (2)	−0.965 (2)	2.0 (8)
S(3)	−0.074 (1)	−0.2744 (5)	−0.6847 (8)	4.3 (3)	C(3)	−0.148 (5)	−0.410 (2)	−0.254 (3)	4.8 (12)
S(4)	−0.100 (2)	−0.1767 (7)	−0.4347 (10)	6.8 (4)	C(4)	−0.157 (4)	−0.317 (2)	−0.618 (2)	2.5 (9)
S(5)	−0.025 (1)	−0.4429 (6)	−0.1729 (9)	4.9 (3)	C(5)	−0.358 (4)	−0.316 (1)	−1.137 (2)	0.9 (7)
S(6)	−0.468 (2)	−0.5395 (7)	−0.9529 (11)	7.1 (4)	C(6)	−0.181 (5)	−0.503 (2)	−0.468 (3)	4.4 (11)
S(7)	−0.099 (2)	−0.5663 (7)	−0.4556 (11)	7.9 (4)	C(7)	−0.174 (5)	−0.237 (2)	−0.416 (3)	3.6 (10)
S(8)	−0.476 (2)	−0.1812 (7)	−0.9614 (10)	6.1 (4)	C(8)	−0.381 (5)	−0.234 (2)	−0.934 (3)	5.2 (12)
O(1)	0.025 (2)	−0.384 (1)	−0.802 (2)	2.7 (5)	C(9)	−0.596 (3)	−0.307 (1)	−0.529 (2)	0.6 (7)
O(2)	0.004 (3)	−0.275 (1)	−0.911 (2)	2.6 (6)	C(10)	0.052 (4)	−0.288 (2)	−0.989 (2)	2.0 (8)
O(3)	−0.544 (3)	−0.296 (1)	−0.446 (2)	2.4 (6)	C(11)	−0.596 (5)	−0.444 (2)	−0.390 (3)	4.2 (11)
O(4)	−0.544 (3)	−0.446 (1)	−0.468 (2)	4.5 (7)	C(12)	0.081 (4)	−0.422 (2)	−0.849 (3)	3.3 (10)
O(5)	−0.086 (3)	−0.923 (1)	−0.459 (2)	4.7 (7)	C(13)	0.153 (5)	−0.237 (2)	−1.017 (3)	3.9 (11)
O(6)	−0.088 (3)	−0.835 (1)	−0.580 (2)	5.0 (7)	C(14)	0.199 (4)	−0.458 (2)	−0.798 (3)	3.1 (10)
O(7)	−0.398 (3)	−0.842 (2)	−0.013 (2)	7.2 (8)	C(15)	0.122 (4)	−0.520 (2)	−0.786 (3)	2.6 (9)
O(8)	−0.199 (3)	−0.844 (1)	−0.763 (2)	5.1 (7)	C(16)	0.259 (6)	−0.557 (2)	−0.747 (3)	5.7 (12)
O(9)	−0.409 (4)	−0.653 (2)	−0.806 (3)	8.6 (11)	C(17)	−0.009 (5)	−0.512 (2)	−0.728 (3)	4.3 (11)
O(10)	−0.415 (5)	−0.091 (2)	−0.479 (3)	11.5 (14)	C(18)	−0.707 (4)	−0.267 (2)	−0.575 (2)	2.1 (8)
O(11)	−0.355 (4)	−0.837 (2)	−0.197 (3)	10.3 (11)	C(19)	−0.705 (5)	−0.482 (2)	−0.347 (3)	4.4 (11)
O(12)	−0.554 (3)	−0.401 (1)	−0.337 (2)	3.2 (6)	C(20)	−0.617 (6)	−0.514 (2)	−0.266 (4)	6.6 (14)
O(13)	0.047 (2)	−0.433 (1)	−0.934 (1)	1.8 (5)	C(21)	−0.478 (7)	−0.536 (3)	−0.290 (4)	9.1 (18)
O(14)	−0.544 (3)	−0.347 (1)	−0.574 (2)	4.1 (6)	C(22)	−0.728 (6)	−0.555 (2)	−0.222 (4)	6.6 (14)
O(15)	0.019 (3)	−0.324 (1)	−1.040 (2)	3.5 (6)	C(23)	−0.098 (6)	−0.566 (2)	−0.741 (3)	5.6 (13)
O(16)	0.310 (5)	0.556 (2)	0.956 (3)	9.9 (12)	C(24)	−0.627 (7)	−0.226 (2)	−0.637 (4)	8.2 (17)
O(17)	0.349 (5)	0.855 (2)	0.604 (3)	12.1 (14)	C(25)	−0.383 (7)	−0.551 (3)	−0.204 (4)	9.6 (19)
N(1)	−0.223 (4)	−0.461 (1)	−0.469 (2)	4.0 (9)	C(26)	0.059 (5)	−0.187 (2)	−1.069 (3)	4.2 (11)
N(2)	−0.297 (3)	−0.390 (1)	−0.798 (2)	2.6 (7)	C(27)	−0.043 (7)	−0.212 (2)	−1.146 (4)	8.1 (16)
N(3)	−0.762 (4)	−0.515 (1)	−0.433 (2)	2.9 (7)	C(28)	−0.035 (11)	−0.161 (4)	−1.017 (7)	16.9 (34)
N(4)	−0.802 (3)	−0.241 (1)	−0.508 (2)	2.9 (7)	C(29)	0.038 (9)	−0.098 (4)	−0.970 (5)	12.7 (24)
N(5)	0.254 (3)	−0.430 (1)	−0.717 (2)	2.5 (7)	C(30)	−0.742 (6)	−0.204 (2)	−0.726 (4)	8.1 (16)
N(6)	0.258 (4)	−0.264 (1)	−1.085 (2)	3.4 (8)	C(31)	−0.474 (10)	−0.212 (4)	−0.651 (6)	16.5 (32)
N(7)	−0.221 (4)	−0.383 (2)	−0.299 (3)	6.9 (11)	C(32)	−0.757 (7)	−0.171 (3)	−0.688 (4)	10.6 (18)
N(8)	−0.230 (3)	−0.282 (1)	−0.407 (2)	2.7 (7)					
N(9)	−0.269 (4)	−0.451 (2)	−0.973 (2)	5.2 (10)					
N(10)	−0.318 (3)	−0.276 (1)	−0.905 (2)	2.5 (7)					
N(10)	−0.211 (4)	−0.353 (1)	−0.577 (2)	3.9 (8)					
N(12)	−0.295 (2)	−0.343 (1)	−1.083 (1)	0.8 (5)					

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

in the range 90.1 (3)–91.8 (4)°, whereas the Mo–Mo′–N angles vary from 100.4 (4) to 103.6 (4)°. The former are typical of all such angles in $Mo_2(O_2CR)$ moieties, and the latter are comparable to those found in $Mo_2Cl_8^{4-}$ ions.[6] The Mo–Mo distances in the two molecules are identical at 2.133 (2) Å. This is slightly longer than the value in the tetraglycinato species,[1] 2.115 (1) Å, and slightly shorter than most of those in $Mo_2X_8^{4-}$ species.[6]

There are so few water molecules in the crystals of this compound that it is pertinent to enquire about the surroundings of the $-NH_3^+$ groups. Each of the glycyl nitrogen atoms is coplanar with the rest of its own glycyl residue, and the distances from N to the nearer carboxyl oxygen atom are all 2.6 ± 0.1 Å. Since our difference Fourier maps did not clearly reveal any of the hydrogen atoms of the $-NH_3^+$ groups, we cannot say whether this coplanarity is favored by the formation of an N–H···O hydrogen bond or by the staggering of the $-NH_3$ group so as to place hydrogen atoms as far from the oxygen atom as possible. In any event, the $-NH_3^+$ groups of molecule II form hydrogen bonds to the water molecules in the cell with distances of N(11)···O(57) = 2.61 Å and N(12)···O(56) = 2.71 Å. In addition, N(11) has thiocyanate sulfur atoms at distances of 3.26, 3.54, and 3.58 Å for S(5), S(2), and S(3), respectively, while N(12) has only one sulfur neighbor within less than 4 Å, namely, S(8) at a distance of 3.55 Å. For molecule I, the $-NH_3^+$ groups have no neighboring water molecules. The only external neighbors within less than 4.0 Å of N(2) are S(1) and S(7) which are at distances of 3.46 and 3.66 Å, respectively. There are four neighboring sulfur atoms, S(3), S(6), S(5) and S(1), for N(5), at distances of 3.21, 3.37, 3.56, and 3.62 Å, respectively. While it seems clear that N···S distances such as 3.21, 3.26, and perhaps even 3.37 Å imply the existence of hydrogen bonds, it is not certain what the mode of interaction is when the N···S distances are in the 3.55–3.65 Å range. Hydrogen bonding, if any, at these distances must be rather weak.

Mo_2(L-isoleu)$_2$(NCS)$_4$·4.5H_2O. There are four molecules in the unit cell belonging to space group $P2_1$, and hence there are again two independent molecules in the asymmetric unit, neither of which possesses any crystallographic symmetry. The two molecules are shown in Figure 2, which also defines the atomic numbering scheme. The atomic positional and thermal parameters are listed in Table IV, and the interatomic distances and angles are given in Table V.

The two crystallographically independent molecules are again essentially identical, and practically identical to the molecules of the glycine compound. The only noticeable difference from the glycine compound is that the Mo–Mo bond length, which has a mean value of 2.150 (5) Å, is slightly longer, though the difference is on the borderline of statistical

Table V. Bond Distances (Å) and Bond Angles (deg) for *cis*-(L-isoleucine)$_2$(NCS)$_4$Mo$_2$

Bond Distances for Molecule I

Mo(1)–Mo(3)	2.154 (5)		
–O(1)	2.16 (2)	Mo(3)–O(13)	2.17 (2)
–O(2)	2.15 (3)	–O(15)	2.08 (3)
–N(2)	2.14 (3)	–N(9)	2.10 (4)
–N(10)	2.11 (3)	–N(12)	2.08 (3)
N(2)–C(1)	1.13 (4)	N(9)–C(2)	1.13 (5)
C(1)–S(2)	1.63 (4)	C(2)–S(6)	1.66 (4)
N(10)–C(8)	1.20 (5)	N(12)–C(5)	1.15 (3)
C(8)–S(8)	1.56 (5)	C(5)–(S1)	1.68 (4)
O(1)–C(12)	1.26 (4)	O(2)–C(10)	1.26 (4)
O(13)–C(12)	1.28 (4)	O(15)–C(10)	1.17 (4)
C(12)–C(14)	1.53 (5)	C(10)–C(13)	1.57 (5)
C(14)–N(5)	1.39 (4)	C(13)–N(6)	1.55 (5)
C(14)–C(15)	1.63 (5)	C(13)–C(26)	1.63 (6)
C(15)–C(16)	1.59 (6)	C(26)–C(27)	1.52 (7)
C(15)–C(17)	1.52 (5)	C(26)–C(28)	1.3 (1)
C(17)–C(23)	1.52 (6)	C(28)–C(29)	1.7 (1)

Bond Distances for Molecule II

Mo(2)–Mo(4)	2.145 (5)		
–O(3)	2.05 (3)	Mo(4)–O(4)	2.05 (3)
–O(12)	2.17 (3)	–O(14)	2.09 (3)
–N(7)	2.04 (5)	–N(1)	2.14 (4)
–N(8)	2.10 (3)	–N(11)	2.10 (4)
N(7)–C(3)	1.11 (5)	N(1)–C(6)	1.09 (5)
C(3)–S(5)	1.75 (6)	C(6)–S(7)	1.67 (5)
N(8)–C(7)	1.18 (5)	N(11)–C(4)	1.16 (4)
C(7)–S(4)	1.62 (5)	C(4)–S(3)	1.62 (4)
O(3)–C(9)	1.29 (4)	O(4)–C(11)	1.26 (5)
O(14)–C(9)	1.26 (4)	O(12)–C(11)	1.33 (5)
C(9)–C(18)	1.50 (5)	C(11)–C(19)	1.51 (6)
C(18)–N(4)	1.48 (4)	C(19)–N(3)	1.53 (5)
C(18)–C(24)	1.54 (6)	C(19)–C(20)	1.58 (6)
C(24)–C(30)	1.64 (7)	C(20)–C(21)	1.49 (7)
C(24)–C(31)	1.4 (1)	C(20)–C(22)	1.55 (7)
C(30)–C(32)	1.1 (8)	C(21)–C(25)	1.46 (8)

Bond Angles for Molecule I

Mo(3)–Mo(1)–O(1)	90.9 (7)	Mo(1)–Mo(3)–O(13)	92.0 (7)
–O(2)	90.3 (7)	–O(15)	91.3 (8)
–N(2)	101.5 (8)	–N(9)	100 (1)
–N(10)	103.6 (8)	–N(12)	101.2 (7)
O(1)–Mo(1)–O(2)	89.8 (9)	O(13)–Mo(3)–O(15)	90.1 (9)
–N(2)	85 (1)	–N(9)	86 (1)
–N(10)	165 (1)	–N(12)	167 (1)
O(2)–Mo(1)–N(2)	167 (1)	O(15)–Mo(3)–N(9)	167 (1)
–N(10)	87 (1)	–N(12)	89 (1)
N(2)–Mo(1)–N(10)	95 (1)	N(9)–Mo(3)–N(12)	93 (1)
S(2)–C(1)–N(2)	170 (4)	S(6)–C(2)–N(9)	179 (4)
S(8)–C(8)–N(10)	172 (5)	S(1)–C(5)–N(12)	177 (3)
Mo(1)–O(1)–C(12)	117 (3)	Mo(1)–O(2)–C(10)	111 (3)
Mo(3)–O(13)–C(12)	115 (3)	Mo(3)–O(15)–C(10)	116 (3)
O(1)–C(12)–O(13)	126 (4)	O(2)–C(10)–O(15)	131 (4)
O(1)–C(12)–C(14)	116 (4)	O(2)–C(10)–C(13)	107 (4)
O(13)–C(12)–C(14)	119 (4)	O(15)–C(10)–C(13)	122 (4)
N(5)–C(14)–C(12)	110 (3)	N(6)–C(13)–C(10)	104 (3)
N(5)–C(14)–C(15)	118 (3)	N(6)–C(13)–C(26)	109 (3)
C(12)–C(14)–C(15)	105 (3)	C(10)–C(13)–C(26)	113 (3)
C(14)–C(15)–C(16)	102 (3)	C(13)–C(26)–C(27)	109 (4)
C(14)–C(15)–C(17)	107 (3)	C(13)–C(26)–C(28)	116 (6)
C(16)–C(15)–C(17)	119 (3)	C(27)–C(26)–C(28)	101 (6)
C(15)–C(17)–C(23)	105 (4)	C(26)–C(28)–C(29)	111 (7)

Bond Angles for Molecule II

Mo(4)–Mo(2)–O(3)	90.4 (7)	Mo(2)–Mo(4)–O(4)	91.7 (9)
–O(12)	89.4 (7)	–O(14)	91.7 (9)
–N(7)	102 (1)	–N(1)	104 (1)
–N(8)	102.1 (8)	–N(11)	102 (1)
O(3)–Mo(2)–O(12)	89 (1)	O(4)–Mo(4)–O(14)	85 (1)
–N(7)	167 (1)	–N(11)	88 (1)
–N(8)	88 (1)	–N(1)	166 (1)
O(12)–Mo(2)–N(7)	93 (1)	O(14)–Mo(4)–N(11)	163 (1)
–N(8)	168 (1)	–N(1)	92 (1)
N(7)–Mo(2)–N(8)	88 (1)	N(1)–Mo(4)–N(11)	90 (1)
S(5)–C(3)–N(7)	171 (5)	S(7)–C(6)–N(1)	173 (5)
S(4)–C(7)–N(8)	177 (4)	S(3)–C(4)–N(11)	171 (4)
Mo(2)–O(3)–C(9)	120 (2)	Mo(4)–O(4)–C(11)	124 (3)
Mo(4)–O(14)–C(9)	117 (2)	Mo(2)–O(12)–C(11)	118 (3)
O(3) –C(9)–O(14)	121 (3)	O(4)–C(11)–O(12)	115 (4)
O(3)–C(9)–C(18)	119 (3)	O(4)–C(11)–C(19)	130 (5)
O(14)–C(9)–C(18)	120 (3)	O(12)–C(11)–C(19)	114 (4)
N(4)–C(18)–C(9)	112 (3)	N(3)–C(19)–C(11)	99 (3)
N(4)–C(18)–C(24)	115 (4)	N(3)–C(19)–C(20)	120 (4)
C(9)–C(18)–C(24)	109 (3)	C(11)–C(19)–C(20)	106 (4)
C(18)–C(24)–C(30)	111 (5)	C(19)–C(20)–C(21)	115 (5)
C(18)–C(24)–C(31)	135 (6)	C(19)–C(20)–C(22)	107 (4)
C(30)–C(24)–C(31)	112 (6)	C(21)–C(20)–C(22)	119 (5)
C(24)–C(30)–C(32)	86 (8)	C(20)–C(21)–C(25)	109 (6)

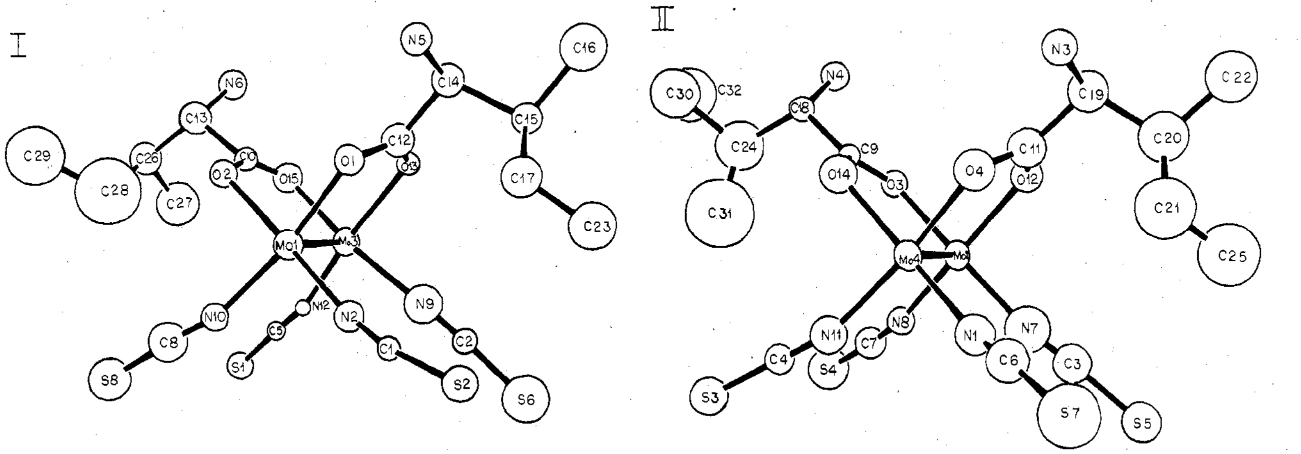

Figure 2. ORTEP projections of the two independent molecules in Mo$_2$(L-isoleu)$_2$(NCS)$_4$·4.5H$_2$O showing the atom numbering used in Tables IV and V.

credibility being slightly less than 3σ.

The structure given in Figure 2 and Tables IV and V contains the correct enantiomorph of the isoleucine molecules. The incorrect enantiomorph of the structure, obtained by inverting all coordinates, refined to give equally plausible bond lengths and angles and only slightly higher residuals, namely, $R_1 = 0.088$ and $R_2 = 0.091$ as compared to values of 0.080 and 0.080, respectively, for the correct enantiomorph.

complex but entirely plausible system of hydrogen bonds to the –NH$_3^+$ groups, with N–H···O distances in the range 2.62–2.79 Å and O–H···O distances of 2.83–2.95 Å. There does not appear to be anything unusual or worthy of detailed discussion here.

In all four of the crystallographically independent molecules examined in this investigation, the nearest axial neighbors of the molybdenum atoms are sulfur atoms. The eight Mo–Mo···S angles vary from 162 to 173° with an average of 169°, and the Mo···S distances vary from 3.035 to 3.236 Å with a mean of 3.108 Å. At these long distances there can be scarcely any donor bonding by sulfur to molybdenum, since Mo–S single bond lengths are typically about 2.45 Å.

Only a few thiocyanato complexes of quadruply bonded M_2 moieties have previously been reported, and only one has been examined by X-ray crystallography, namely, $Mo_2(Ph_2PCH_2PPh_2)_2(NCS)_4$.[7] The thiocyanate ions were shown to be linear and N bonded (mean Mo–N distance = 2.06 Å), and infrared data have suggested that this is true in other cases as well.[8-11]

Compounds of Mo_2^{4+} and Re_2^{6+} containing two bridging ligands and four unidentate ligands have also been reported before. Two stereochemical arrangements have been observed. A transoid arrangement, first observed in $Re_2(O_2CPh)_2I_4$,[12] has been frequently seen subsequently, and a cisoid arrangement, first observed in $Re_2(O_2CCH_3)_2Cl_4$,[13] has not been reported subsequently. Thus, these molecules have structures of a type that has previously been uncommon. The factors which might favor the cisoid and transoid arrangements are obscure.

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Registry No. **1**, 69596-93-6; **2**, 69532-08-7; $K_4Mo_2Cl_8$, 25448-39-9.

Supplementary Material Available: Tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Notes

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Activation Parameters in Electron-Transfer Reactions. The System $Co(phen)_3^{3+}$–Ferrocene in Water/Propan-1-ol Mixture

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Among the several theories available for treating the outer-sphere electronic-transfer reactions,[1] the Marcus theory[2] is the most useful, allowing the calculation of cross-reaction activation free energy (ΔG^*_{12}) through eq 1.

$$\Delta G^*_{12} = w_{12} + \frac{\lambda_{12}}{4}\left(1 + \frac{\Delta G^\circ_{12}{}'}{\lambda_{12}}\right)^2 \qquad (1)$$

$k_{12} = Z \exp(-\Delta G^*_{12}/RT)$ (k_{12} is the cross-reaction rate constant, Z the collision frequency in solution, assumed 10^{11} M^{-1} s^{-1}), $\Delta G^\circ_{12}{}' = \Delta G^\circ + w_{21} - w_{12}$, w_{12} and w_{21} being the work terms involved in bringing together the reactants and products, respectively; λ_{12} equals $2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22})$, where ΔG^*_{11} and ΔG^*_{22} represent the self-exchange activation energies and w_{11} and w_{22} the related work terms.

For reactions in which the work terms are negligible (e.g., when at least one of the reactants is uncharged or the medium is at high ionic strength) and the free energy variation is small, the expression is greatly simplified, giving eq 2, where K_{12} is

$$k_{12} \simeq (k_{11}k_{22}K_{12})^{1/2} \qquad (2)$$

the equilibrium constant and k_{11} and k_{22} are the two self-exchange rate constants.

Recently, Marcus and Sutin[3] showed that the activation parameters for an electron-transfer reaction can be derived by differentiating eq 1 with respect to temperature[4] (eq 3–5).

$$\Delta H^*_{12} = \left(\frac{\Delta H^*_{11}}{2} + \frac{\Delta H^*_{22}}{2}\right)(1 - 4\alpha^2) + \frac{\Delta H^\circ_{12}}{2}(1 + 2\alpha) \qquad (3)$$

$$\Delta S^*_{12} = \left(\frac{\Delta S^*_{11}}{2} + \frac{\Delta S^*_{22}}{2}\right)(1 - 4\alpha^2) + \frac{\Delta S^\circ_{12}}{2}(1 + 2\alpha) \qquad (4)$$

$$\alpha = \Delta G^\circ_{12}/4(\Delta G^*_{11} + \Delta G^*_{22}) \qquad (5)$$

Equations 3–5 have recently received some experimental verification,[5] and, while in some cases there is a good agreement, in other systems the difference between the calculated and experimental enthalpies is within 2–3 kcal mol^{-1} and for the entropies within 10 cal deg^{-1} mol^{-1}. Explanations which account for these discrepancies have been advanced.[5a]

The application of the Marcus equations is also sometimes limited, by the uncertainty in some of the parameters and by the difficulty in the evaluation of the work terms.[6] The importance of the data reliability has been recently underlined by Wherland and Gray.[7]

In order to test with more accuracy the application of eq 1–5, we have decided to investigate reactions 6 and 7 in 50:50

$$Co(phen)_3^{3+} + Fe(cp)_2 \rightleftharpoons Co(phen)_3^{2+} + Fe(cp)_2^+ \qquad (6)$$

$$Co(phen)_3^{3+} + Fe(mcp)_2 \rightleftharpoons Co(phen)_3^{2+} + Fe(mcp)_2^+ \qquad (7)$$

v/v water/propan-1-ol. In fact the self-exchange rate constants and related activation parameters can be calculated for $Fe(cp)_2^{+/0}$ system in the present medium,[8] the analogous data for $Co(phen)_3^{3+/2+}$ can be determined by polarimetry, and the equilibrium quotients for reaction 6 can be obtained spectrophotometrically at different temperatures.

Furthermore, since the terms w_{12} and w_{22} can be neglected when one reactant is uncharged, these systems are particularly versatile for the application of the Marcus equations.

Experimental Section

Materials. $Co(phen)_3(ClO_4)_3$[9] and $(+)Co(phen)_3(ClO_4)_3$[10] were prepared according to the literature procedure. $Co(phen)_3^{2+}$ was prepared in situ by the reaction of $Co(NO_3)_2$ with excess phenanthroline (from 3.2 up to 10 molar ratio). Ferrocenes were Alfa products. All other chemicals were of the highest quality available. Doubly distilled water was used.

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