Inorg. Chem. **1980**, *19*, 1215-1221

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Crystal Structure and Polarized, Low-Temperature Electronic Absorption Spectrum of Tetrakis(L-leucine)dimolybdenum(II) Dichloride Bis(*p*-toluenesulfonate) Dihydrate

AVI BINO, F. ALBERT COTTON,* and PHILLIP E. FANWICK

Received August 24, 1979

The $[Mo_2(L\text{-leucine})_4]^{4+}$ ion has been obtained in crystals of the title compound, and its structure and electronic absorption spectrum have been studied. The compound crystallizes in the monoclinic space group $P2_1$ with unit cell dimensions $a = 12.557$ (3) Å, $b = 29.938$ (7) Å, $c = 14.532$ (6) Å, $\beta = 92.09$ (2)°, and $Z = 4$. Two formula units constitute the crystallographic asymmetric unit. The correct enantiomorph, shown by comparison to the known absolute configuration of L-leucine, was refined. The two $[Mo_2(L\text{-leucine})_4]^{4+}$ ions have essentially identical dimensions (e.g., D(Mo–Mo) = 2.108 (1) and 2.111 (1) Å) and are arranged in the crystal so that their Mo–Mo axes are parallel within experimental error. The absorption spectrum in the region of the $\delta^* \leftarrow \delta$ transition has been measured on the 010 face of a single crystal at 5 K by using polarized light. The measured spectra with polarizations relative to crystal axes have been resolved and replotted in the form of spectra polarized $\parallel$ and $\perp$ to the molecular (Mo–Mo) axis. There is an extremely close resemblance to the polarized spectra which were previously reported for $Mo_2(gly)_4(SO_4)_2 \cdot 4H_2O$ but which lacked the presence of an "extra" z-polarized vibrational progression. This confirms the previous suggestion of Martin, Newman, and Fanwick that this "extra" progression is caused by an impurity. It is concluded that the $\delta^* \leftarrow \delta$ assignment is consistent with all known experimental data.

Introduction

In recent years the electronic spectra of complexes of quadruply bonded dimetal systems have been extensively studied. Particular attention has been paid to the lowest energy absorption band, which can be assigned to the $\delta^* \leftarrow \delta$ transition. From studies of polarized crystal spectra, the $\delta^* \leftarrow \delta$ assignment of the transition has been made, unambiguously, for $[Re_2Cl_8]^{2-}$,[1] $[Mo_2Cl_8]^{4-}$,[2] and $[Mo_2(SO_4)_4]^{4-}$.[3] However, the tetracarboxylates of molybdenum have presented difficulties.

The first study of the crystal spectrum of a compound of the type $Mo_2(O_2CR)_4$ was done on the tetraglycine complex[4] $[Mo_2(O_2CCH_2NH_2)_4]^{4+}$ in the form of its sulfate. This crystal appeared to be ideal because of the high tetragonal crystal symmetry with the crystal c axis being identical with the metal–metal axis. In addition, the dimolybdenum species occupied sites of symmetry which was nearly as high ($\bar{4}$) as the idealized symmetry (D_{4h}) of the isolated complex. The weak, lowest energy transition at ca. 20 000 cm^{-1} was examined closely and found to display vibrational fine structure. Two completely z-polarized progressions and two completely xy-polarized progressions were observed. All four progressions were based on a frequency of 344 cm^{-1}, which was assigned as the metal–metal stretching frequency in the excited state. The first z-polarized origin, at 20 570 cm^{-1}, was 940 cm^{-1} from the next origin. It was suggested at the time that this first progression represented a transition that was forbidden in the idealized D_{4h} symmetry but allowed in the actual S_4 crystallographic symmetry. The other z-polarized progression and the two xy-polarized progressions were assigned to vibronically allowed transitions involving the same electronic excitation.

The spectra of $Mo_2(O_2CH)_4$[3] and $Mo_2(O_2CCH_3)_4$[5,6] were studied later and had some features that were similar. Both of these compounds displayed three strong vibrational progressions, each based on the same frequency, with two polarized in one direction and the third in the other. The frequency was consistent with that expected for ν(Mo–Mo) in the excited state. Other weaker progressions were also observed. However, for both the formato and acetato compounds there was one feature that was drastically different from the glycinato case: the oriented gas polarization ratios were not observed. In fact a variety of polarization ratios for different progressions was seen. This led Trogler et al.[5] to assume that the transition was to an orbital that would be degenerate in D_{4h} symmetry, thus giving xy polarization, and that the degeneracy was being removed because of intermolecular interactions and lower site symmetry. They assigned this band to the Laporte-forbidden $\pi^* \leftarrow \delta$ transition.

Martin et al.[6] have recently reinvestigated the crystal spectrum of $Mo_2(O_2CCH_3)_4$. They found that a variety of unusual effects had to be taken into consideration to obtain a correct assignment. These included the extremely unfavorable crystal optics of the triclinic crystals and the possibility of Herzberg–Teller coupling of weak dipole-allowed transitions which would further alter the direction of the transition moment. After studies of the "hot bands" and a least-squares determination of the transition-moment direction, it was concluded that the spectra justified an assignment as the $\delta^* \leftarrow \delta$ transition. It was further suggested that the first z-polarized progression in the tetraglycine spectrum was probably due to the presence of an impurity, possibly involving coordinated sulfate anions.

In view of these earlier complications, we felt that another study of an (amino acid)$_4$Mo$_2$ complex would be worthwhile. It was hoped that a simpler and more general case than the previous glycinato complex would be obtained, and attempts were first made to prepare different crystals of the $[Mo_2(O_2CCH_2NH_3)_4]^{4+}$ ion. While two crystalline polymorphs of $[Mo_2(O_2CCH_2NH_3)_4]Cl_4$ were obtained,[7] neither proved suitable for crystal spectroscopy. With leucine we were able to obtain the crystalline compound $Mo_2(L\text{-leucine})_4Cl_2(pts)_2 \cdot 2H_2O$, where pts stands for the p-toluenesulfonate ion. The crystal structure and the spectrum of this compound are reported here.

Experimental Section

Preparation. $K_4Mo_2Cl_8$ (0.05 g), prepared by a literature method,[8a] was dissolved in 20 mL of a saturated solution of L-leucine in HCl (0.1 M). The yellow solution of the tetracarboxylato complex was allowed to mix by diffusion through a glass frit with a 1 M solution

---

[1] Cowman, C. D.; Gray, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8177.

[2] Fanwick, P. E; Martin, D. S.; Cotton, F. A.; Webb, T. R. *Inorg. Chem.* **1977**, *16*, 2103.

[3] Cotton, F. A.; Martin, D. S.; Fanwick, P. E.; Peters, T. J.; Webb, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 4681.

[4] Cotton, F. A.; Martin, D. S.; Webb, T. R.; Peters, T. J. *Inorg. Chem.* **1976**, *15*, 1199.

[5] Trogler, W. C.; Solomon, E. J.; Trajberg, I.; Ballhausen, C. J.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *16*, 828.

[6] Martin, D. S.; Newman, R. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2511.

[7] Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 1719.

[8] (a) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 351. (b) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Ibid.* **1979**, *18*, 3558.

0020-1669/80/1319-1215$01.00/0 © 1980 American Chemical Society

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}
Mo(1)	0.06736 (8)	0.50977 (0)	0.57829 (7)	2.60 (4)	2.20 (4)	2.26 (4)	−0.26 (4)	0.12 (4)	−0.06 (4)
Mo(2)	0.08469 (8)	0.55712 (4)	0.47223 (7)	2.82 (4)	2.51 (5)	2.20 (4)	−0.31 (5)	0.11 (4)	0.13 (4)
Mo(3)	0.41761 (8)	0.06193 (4)	0.06808 (7)	2.18 (4)	2.27 (4)	2.33 (4)	−0.08 (4)	0.11 (3)	−0.09 (4)
Mo(4)	0.39306 (8)	0.01514 (4)	0.96097 (7)	2.07 (4)	2.44 (5)	2.23 (4)	−0.03 (4)	−0.02 (3)	−0.01 (4)
Cl(1)	0.0683 (3)	0.4419 (1)	0.7144 (2)	3.2 (1)	3.0 (1)	3.0 (1)	−0.2 (1)	0.0 (1)	0.3 (1)
Cl(3)	0.4222 (3)	0.1302 (1)	0.2053 (3)	3.5 (1)	3.2 (2)	3.7 (2)	−0.1 (1)	0.2 (1)	−0.4 (1)
Cl(2)	0.0285 (3)	0.0862 (2)	0.1232 (3)	4.2 (2)	5.1 (2)	3.8 (2)	−0.0 (2)	−0.0 (1)	0.1 (2)
Cl(4)	0.4583 (3)	0.4795 (2)	0.6463 (3)	5.1 (2)	4.8 (2)	4.3 (2)	−0.3 (2)	1.0 (2)	−0.2 (2)
S(20)	0.4558 (3)	0.9395 (1)	0.7670 (2)	3.3 (1)	3.9 (2)	2.7 (1)	0.5 (1)	0.5 (1)	−0.3 (1)
S(30)	0.0998 (3)	0.6349 (1)	0.2862 (3)	3.8 (2)	3.9 (2)	3.3 (2)	−0.0 (1)	0.4 (1)	0.3 (1)
S(40)	0.0226 (3)	0.4662 (2)	0.1127 (3)	3.7 (2)	4.5 (2)	4.7 (2)	−0.6 (2)	0.1 (2)	0.9 (2)
S(50)	0.4572 (4)	0.0972 (2)	0.5733 (3)	6.1 (2)	8.2 (3)	3.8 (2)	2.9 (2)	−0.5 (2)	−0.4 (2)
O(11)	0.0503 (6)	0.0493 (3)	0.3612 (5)	2.6 (3)	2.4 (4)	2.0 (3)	−0.1 (3)	0.3 (3)	−0.2 (3)
O(12)	0.0552 (7)	0.9763 (3)	0.4955 (6)	3.8 (4)	2.9 (4)	2.3 (4)	0.8 (4)	−0.5 (3)	0.0 (3)
O(13)	0.1858 (7)	0.5421 (3)	0.6630 (6)	2.8 (4)	3.3 (4)	2.5 (4)	−0.8 (3)	−0.8 (3)	0.5 (3)
O(14)	0.1851 (7)	0.4692 (3)	0.5215 (6)	4.5 (4)	2.1 (4)	2.8 (4)	0.3 (4)	0.6 (4)	−0.0 (3)
O(21)	0.0324 (7)	0.0993 (3)	0.4716 (6)	3.1 (4)	2.8 (4)	2.8 (4)	−0.4 (3)	0.5 (3)	−0.2 (3)
O(22)	0.0353 (7)	0.0240 (3)	0.6097 (6)	3.5 (4)	4.2 (5)	2.7 (4)	1.6 (4)	−0.4 (3)	−0.1 (4)
O(23)	0.2052 (7)	0.5919 (3)	0.5501 (6)	3.6 (4)	3.2 (4)	2.8 (4)	−0.6 (4)	−0.1 (3)	−0.1 (4)
O(24)	0.2066 (7)	0.5191 (4)	0.4130 (6)	3.5 (4)	4.4 (5)	2.1 (4)	0.5 (4)	0.6 (3)	0.3 (4)
O(31)	0.5298 (6)	0.0976 (3)	−0.0070 (6)	2.5 (3)	2.9 (4)	2.8 (4)	−1.1 (3)	−0.2 (3)	−0.4 (3)
O(32)	0.3078 (7)	0.0275 (3)	0.1510 (6)	2.9 (4)	2.4 (4)	3.3 (4)	0.1 (3)	0.5 (3)	0.1 (3)
O(33)	0.4555 (6)	0.5229 (3)	0.8721 (5)	2.2 (3)	3.1 (4)	2.2 (3)	0.2 (3)	−0.8 (3)	−0.5 (3)
O(34)	0.2917 (6)	0.1025 (3)	0.0096 (6)	2.0 (3)	3.1 (4)	3.4 (4)	−0.2 (3)	−0.0 (3)	0.4 (4)
O(41)	0.5019 (6)	0.0495 (3)	0.8778 (6)	2.9 (3)	2.4 (4)	2.8 (4)	−0.6 (3)	0.2 (3)	0.1 (3)
O(42)	0.2786 (6)	0.9784 (3)	0.0365 (6)	2.3 (3)	3.0 (4)	2.8 (4)	−0.2 (3)	0.5 (3)	−0.2 (3)
O(43)	0.4828 (7)	0.4737 (3)	0.9834 (6)	2.5 (3)	2.6 (4)	3.0 (4)	−0.9 (3)	−0.2 (3)	0.1 (3)
O(44)	0.2687 (6)	0.0511 (3)	0.8994 (6)	2.5 (3)	3.5 (4)	2.8 (4)	−0.4 (3)	−0.4 (3)	0.0 (4)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(201)	0.4414 (8)	0.4602 (4)	0.2152 (7)	3.9 (2)	C(202)	0.4541 (15)	0.8501 (7)	0.7286 (13)	5.6 (4)
O(202)	0.3742 (7)	0.9575 (3)	0.8269 (7)	3.6 (2)	C(203)	0.4736 (17)	0.8039 (8)	0.7507 (15)	7.0 (5)
O(203)	0.4215 (8)	0.9419 (3)	0.6712 (7)	3.9 (2)	C(204)	0.4964 (16)	0.2925 (7)	0.1588 (14)	6.2 (4)
O(301)	0.1148 (8)	0.6302 (4)	0.1870 (7)	4.5 (2)	C(205)	0.4759 (18)	0.3253 (8)	0.0957 (16)	7.2 (5)
O(302)	0.1948 (10)	0.6234 (5)	0.3372 (9)	6.0 (3)	C(206)	0.5044 (17)	0.8724 (7)	0.8822 (15)	6.6 (5)
O(303)	0.0067 (10)	0.6107 (5)	0.3127 (9)	6.7 (3)	C(207)	0.4716 (20)	0.2436 (9)	0.1366 (18)	8.7 (6)
O(401)	0.0608 (11)	−0.0062 (5)	0.8545 (10)	6.9 (3)	C(211)	0.4549 (10)	0.5814 (5)	0.0867 (9)	2.9 (3)
O(402)	0.0501 (10)	0.4790 (5)	0.0203 (9)	6.7 (3)	C(212)	0.3708 (11)	0.6077 (5)	0.1419 (10)	3.4 (3)
O(403)	0.1126 (10)	0.4619 (5)	0.1743 (9)	6.0 (3)	C(213)	0.4112 (12)	0.6542 (6)	0.1761 (11)	4.2 (3)
O(501)	0.4583 (13)	0.5754 (6)	0.4728 (12)	9.6 (5)	C(214)	0.4243 (15)	0.6898 (7)	0.0997 (13)	5.8 (4)
O(502)	0.3554 (11)	0.0945 (5)	0.5265 (10)	7.3 (3)	C(215)	0.4485 (18)	0.7339 (9)	0.1475 (17)	8.1 (6)
O(503)	0.4600 (12)	0.0799 (6)	0.6664 (11)	8.5 (4)	C(216)	0.3168 (20)	0.6917 (9)	0.0397 (19)	8.9 (7)
Ow(1)	0.3144 (10)	0.0248 (4)	0.3912 (9)	6.0 (3)	C(221)	0.2632 (10)	−0.0059 (4)	0.1167 (9)	2.6 (2)
Ow(2)	0.2848 (10)	0.5075 (5)	0.1066 (9)	6.8 (3)	C(222)	0.1810 (10)	0.9692 (5)	0.1737 (9)	2.8 (3)
Ow(3)	0.2096 (10)	0.5485 (5)	0.9158 (9)	6.1 (3)	C(223)	0.1881 (13)	0.9171 (6)	0.1610 (12)	4.5 (3)
Ow(4)	0.2082 (11)	0.0883 (6)	0.6721 (10)	7.6 (4)	C(224)	0.3020 (14)	0.9001 (7)	0.1960 (13)	5.3 (4)
N(111)	0.2130 (9)	0.0913 (4)	0.2834 (8)	3.1 (2)	C(225)	0.3139 (20)	0.8514 (10)	0.1598 (18)	9.2 (7)
N(121)	0.2019 (11)	−0.0033 (5)	0.7092 (10)	4.6 (3)	C(226)	0.3133 (19)	0.9008 (9)	0.3036 (17)	8.4 (6)
N(131)	0.4190 (9)	0.5823 (4)	0.6614 (8)	3.4 (2)	C(231)	0.4343 (9)	0.4874 (4)	0.9130 (8)	2.0 (2)
N(141)	0.4207 (9)	0.4808 (4)	0.4328 (8)	3.7 (2)	C(232)	0.3422 (11)	0.4574 (5)	0.8776 (10)	3.2 (3)
N(211)	0.3472 (9)	0.5786 (4)	0.2238 (8)	3.8 (3)	C(233)	0.3860 (11)	0.4114 (5)	0.8470 (10)	3.2 (3)
N(221)	0.0740 (10)	0.9839 (4)	0.1418 (9)	4.0 (3)	C(234)	0.2983 (13)	0.3788 (6)	0.8156 (12)	4.8 (4)
N(231)	0.2850 (8)	0.4811 (4)	0.8000 (7)	2.8 (2)	C(235)	0.3501 (19)	0.3363 (9)	0.7848 (17)	8.2 (6)
N(241)	0.0548 (9)	0.0867 (4)	0.9102 (8)	3.2 (2)	C(236)	0.2197 (17)	0.3698 (8)	0.8891 (15)	7.3 (5)
					C(241)	0.2442 (10)	0.0870 (5)	0.9378 (9)	2.9 (3)
C(111)	0.0752 (10)	0.0849 (4)	0.3987 (9)	2.5 (2)	C(242)	0.1508 (10)	0.1145 (5)	0.8958 (9)	2.9 (3)
C(112)	0.1598 (11)	0.1161 (5)	0.3599 (10)	3.6 (3)	C(243)	0.1359 (13)	0.1614 (6)	0.9357 (12)	4.7 (4)
C(113)	0.1098 (10)	0.1600 (5)	0.3263 (9)	2.9 (3)	C(244)	0.2277 (18)	0.1951 (8)	0.9091 (16)	7.5 (6)
C(114)	0.1895 (13)	0.1938 (6)	0.2910 (12)	4.9 (4)	C(245)	0.1999 (21)	0.2374 (10)	0.9548 (20)	9.4 (7)
C(115)	0.1268 (17)	0.2345 (8)	0.2530 (16)	7.2 (5)	C(246)	0.2309 (23)	0.2055 (11)	0.8113 (21)	10.5 (8)
C(116)	0.2758 (19)	0.2087 (9)	0.3621 (18)	8.3 (6)	C(301)	0.0707 (12)	0.6907 (6)	0.3068 (11)	4.1 (3)
C(121)	0.0794 (11)	0.9904 (5)	0.5754 (10)	3.2 (3)	C(302)	0.9691 (17)	0.2025 (8)	0.6052 (15)	6.9 (5)
C(122)	0.1743 (12)	0.9705 (5)	0.6276 (11)	4.0 (3)	C(303)	0.0032 (21)	0.7467 (10)	0.4087 (19)	9.1 (7)
C(123)	0.1394 (14)	0.9221 (6)	0.6641 (12)	5.0 (4)	C(304)	0.9760 (17)	0.2795 (8)	0.6565 (15)	7.0 (5)
C(124)	0.1202 (14)	0.8863 (6)	0.5914 (12)	5.2 (4)	C(305)	0.0585 (17)	0.7692 (8)	0.2598 (16)	7.3 (5)
C(125)	0.0907 (19)	0.8437 (9)	0.6392 (17)	8.3 (6)	C(306)	0.0885 (17)	0.7210 (8)	0.2360 (15)	7.0 (5)
C(126)	0.2150 (20)	0.8808 (9)	0.5291 (17)	8.7 (7)	C(307)	0.9916 (22)	0.8302 (10)	0.3631 (20)	9.7 (7)
C(131)	0.2285 (10)	0.5766 (4)	0.6295 (9)	2.5 (2)	C(401)	0.9651 (12)	0.4131 (5)	0.1003 (10)	3.8 (3)
C(132)	0.3124 (10)	0.6014 (5)	0.6879 (9)	3.0 (3)	C(402)	0.1415 (14)	0.9062 (7)	0.8988 (13)	5.4 (4)
C(133)	0.3110 (13)	0.6507 (6)	0.6752 (12)	4.6 (4)	C(403)	0.1869 (16)	0.8633 (7)	0.9119 (14)	6.4 (5)
C(134)	0.2054 (15)	0.6732 (7)	0.7064 (14)	6.1 (4)	C(404)	0.1138 (20)	0.8286 (10)	0.9229 (19)	9.0 (7)
C(135)	0.1999 (20)	0.7230 (9)	0.6714 (18)	8.7 (6)	C(405)	0.0081 (19)	0.8318 (8)	0.9169 (17)	7.9 (6)
C(136)	0.1975 (20)	0.6694 (9)	0.8079 (18)	8.7 (6)	C(406)	0.0425 (18)	0.3770 (9)	0.0912 (16)	7.9 (6)
C(141)	0.2299 (10)	0.4828 (5)	0.4494 (9)	2.9 (3)	C(407)	0.1599 (26)	0.7777 (12)	0.9377 (24)	12.7 (10)
C(142)	0.3208 (11)	0.4563 (5)	0.4091 (10)	3.5 (3)	C(501)	0.5010 (15)	0.6533 (7)	0.4234 (13)	5.8 (4)

Table I (*Continued*)

C(143)	0.3340 (12)	0.4087 (5)	0.4439 (10)	3.8 (3)	C(502)	0.4065 (18)	0.1871 (9)	0.5870 (16)	8.0 (6)
C(144)	0.2386 (15)	0.3772 (7)	0.4147 (13)	5.7 (4)	C(503)	0.4402 (20)	0.2318 (9)	0.5841 (18)	9.0 (7)
C(145)	0.2570 (23)	0.3336 (11)	0.4586 (21)	10.7 (8)	C(504)	0.4479 (18)	0.7443 (9)	0.4200 (17)	8.2 (6)
C(146)	0.2415 (20)	0.3714 (9)	0.3121 (17)	8.7 (6)	C(505)	0.3727 (19)	0.7089 (9)	0.4276 (17)	8.4 (6)
C(201)	0.5261 (11)	0.3827 (5)	0.2060 (10)	3.7 (3)	C(506)	0.4012 (17)	0.6663 (8)	0.4289 (16)	7.3 (5)
					C(507)	0.4121 (28)	0.7967 (13)	0.4208 (25)	13.5 (11)

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

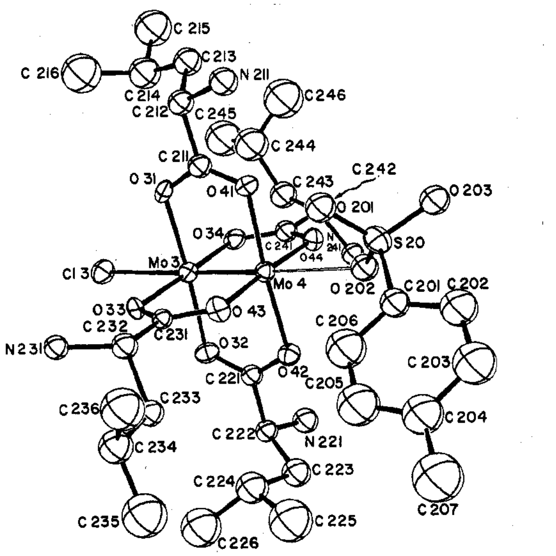

Figure 1. ORTEP drawing of one of the crystallographically independent $[Mo_2(L\text{-leucine})_4]^{4+}$ ions.

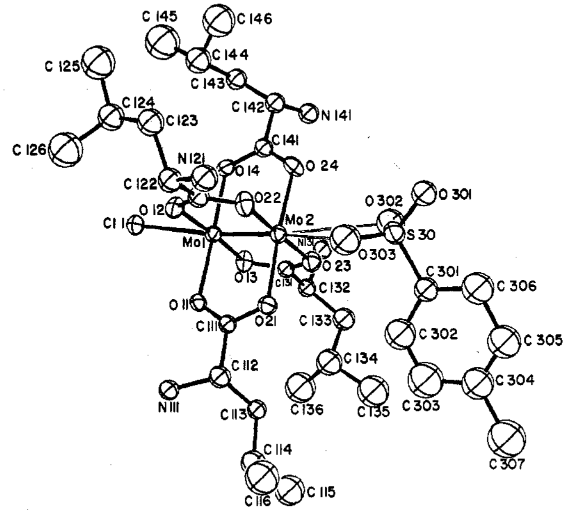

Figure 2. ORTEP drawing of the second crystallographically independent $[Mo_2(L\text{-leucine})_4]^{4+}$ ion.

of *p*-toluenesulfonic acid at 25 °C. Yellow crystals were formed over a period of 10 h.

X-ray Crystallography. A crystal of dimensions 0.10 × 0.15 × 0.15 mm was attached to the end of a glass fiber and mounted on an Enraf-Nonius CAD-4F automatic diffractometer. Molybdenum Kα radiation (λ = 0.710 730 Å), with a graphite crystal monochromator in the incident beam, was used. Preliminary examination showed that the crystal belonged to the monoclinic system, space group $P2_1$. The unit cell dimensions, a = 12.557 (3) Å, b = 29.938 (7) Å, c = 14.532 (6) Å, β = 92.09 (2)°, and V = 5459 (1) Å^3, were obtained by a least-squares fit of 25 reflections in the range $12° < \theta < 15°$. Data were measured by using an ω–2θ motion. A total of 7409 reflections in the range $3° < 2\theta < 45°$ were collected, 6254 of which having $I > 3\sigma(I)$ were used to solve and refine the structure. General procedures for data collection have been described elsewhere.[8b] The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is only 6.87 cm^{-1}, and no absorption correction was applied.

The heavy-atom positions were obtained by direct methods with the MULTAN program. The structure was refined[9] in space group $P2_1$ to convergence by using anisotropic thermal parameters for all molybdenum, chlorine, and sulfur atoms and for all oxygen atoms in the coordination sphere. Isotropic thermal parameters were used for the remaining nonhydrogen atoms. The absolute configurations at the leucines were found to be correct.

The discrepancy indices, defined as

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

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

had final values of R_1 = 0.059 and R_2 = 0.082, and the goodness of fit parameter was equal to 2.18. The final difference map showed no peaks of structural significance. A list of observed and calculated structure factors is available as supplementary material.

Spectra. Crystal spectra were recorded on a Cary 17-D spectrophotometer by using equipment and methods that have been previously described.[10]

Results and Discussion

Structure. There are two formula units in the asymmetric unit. Thus, there are two crystallographically independent $[Mo_2(L\text{-leucine})_4]^{4+}$ units, neither having any crystallographically imposed symmetry. The atomic positional and thermal parameters are listed in Table I. Each of the Mo_2^{4+} complexes is displayed in Figures 1 and 2 where the atomic numbering scheme is defined. The interatomic distances and angles are listed in Table II. At the top of parts A and B of this table the distances and angles involving the molybdenum atoms and those atoms bound to them are listed side by side for the two separate complexes. It can be seen that the dimensions are essentially the same for both. In each one the arrangement of axial ligands is unsymmetrical, with a Cl^- ion at one end and two sulfonate oxygen atoms at the other.

The Mo–Mo distances are the same within experimental error, the mean value being 2.110 (1) Å. These dimensions are all very similar to those found in many other $Mo_2(O_2CR)_4$ structures.[11] It is especially important with respect to the spectroscopic phase of this work to note that the two Mo–Mo axes are parallel to within experimental error. Thus, in effect, all four molecules in this unit cell are equivalent in dimensions and orientation.

Spectrum. The spectrum for polarized light entering through the 010 face of a thin (~10 nm) crystal is shown in Figure 3. The same crystal was subsequently aligned on the diffractometer and indexed, and the above identification of the face was conclusively verified. The extinction directions were determined to be nearly parallel and perpendicular to the crystal a axis. In principle, the 010 face can present problems because the extinction direction may change with wavelength. Moreover, since the space group $P2_1$ is acentric,

---

(9) All computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, using a locally modified version of the Enraf-Nonius structure determination package.

(10) (a) Cotton, F. A.; Fanwick, P. E. *J. Am. Chem. Soc.* **1979**, *101*, 5252. (b) Cotton, F. A.; Fanwick, P. E.; Gage, L. D., *J. Am. Chem. Soc.* **1980**, *102*, 1570.

(11) Bino, A.; Cotton, F. A., paper presented at the Third International Conference on the Chemistry and Uses of Molybdenum, Ann Arbor, MI, Aug 1979.

Table II. Bond Distances (Å) and Angles (Deg)

A. Bond Distances

Mo(1)–Mo(2)	2.111 (1)	Mo(3)–Mo(4)	2.108 (1)	C(132)–C(133)	1.49 (2)	C(232)–C(233)	1.56 (2)
Mo(1)–O(11)	2.109 (6)	Mo(3)–O(31)	2.104 (6)	C(132)–N(131)	1.52 (1)	C(232)–N(231)	1.49 (1)
–O(12)	2.098 (6)	–O(32)	2.130 (6)	C(133)–C(134)	1.56 (2)	C(233)–C(234)	1.53 (2)
–O(13)	2.129 (6)	–O(33)	2.136 (6)	C(134)–C(135)	1.60 (2)	C(234)–C(235)	1.51 (2)
–O(14)	2.106 (7)	–O(34)	2.145 (6)	C(134)–C(136)	1.49 (2)	C(234)–C(236)	1.51 (2)
–Cl(1)	2.836 (3)	–Cl(3)	2.855 (3)	C(141)–C(142)	1.53 (2)	C(241)–C(242)	1.54 (1)
Mo(2)–O(21)	2.124 (6)	Mo(4)–O(41)	2.124 (6)	C(142)–C(143)	1.52 (2)	C(242)–C(243)	1.53 (2)
–O(22)	2.130 (6)	–O(42)	2.144 (6)	C(142)–N(141)	1.48 (1)	C(242)–N(241)	1.49 (1)
–O(23)	2.129 (6)	–O(43)	2.128 (6)	C(143)–C(144)	1.57 (2)	C(243)–C(244)	1.59 (2)
–O(24)	2.117 (7)	–O(44)	2.073 (6)	C(144)–C(145)	1.47 (3)	C(244)–C(245)	1.48 (3)
–O(303)	2.956 (7)	–O(202)	2.608 (7)	C(144)–C(146)	1.50 (2)	C(244)–C(246)	1.46 (3)
–O(302)	3.126 (7)	–O(201)	3.737 (7)	S(20)–O(201)	1.447 (8)	S(40)–O(401)	1.43 (1)
O(11)–C(111)	1.23 (1)	O(31)–C(211)	1.28 (1)	–O(202)	1.470 (8)	–O(402)	1.45 (1)
O(21)–C(111)	1.28 (1)	O(41)–C(211)	1.21 (1)	–O(203)	1.444 (8)	–O(403)	1.422 (9)
O(21)–C(121)	1.26 (1)	O(32)–C(221)	1.24 (1)	–C(201)	1.76 (1)	–C(401)	1.75 (1)
O(22)–C(121)	1.26 (1)	O(42)–C(221)	1.28 (1)	S(30)–O(301)	1.466 (8)	S(50)–O(501)	1.43 (1)
O(13)–C(131)	1.27 (1)	O(33)–C(231)	1.25 (1)	–O(302)	1.424 (9)	–O(502)	1.43 (1)
O(23)–C(131)	1.27 (1)	O(43)–C(231)	1.24 (1)	–O(303)	1.44 (1)	–O(503)	1.45 (1)
O(14)–C(141)	1.28 (1)	O(34)–C(241)	1.27 (1)	–C(301)	1.74 (1)	–C(501)	1.76 (2)
O(24)–C(141)	1.24 (1)	O(44)–C(241)	1.26 (1)	C(201)–C(202)	1.38 (2)	C(401)–C(402)	1.36 (2)
C(111)–C(112)	1.54 (1)	C(211)–C(212)	1.56 (2)	–C(206)	1.36 (2)	–C(406)	1.46 (2)
C(112)–C(113)	1.53 (2)	C(212)–C(213)	1.56 (2)	C(202)–C(203)	1.44 (2)	C(402)–C(403)	1.41 (2)
C(112)–N(111)	1.51 (1)	C(212)–N(211)	1.51 (1)	C(203)–C(204)	1.40 (2)	C(403)–C(404)	1.40 (2)
C(113)–C(114)	1.53 (2)	C(213)–C(214)	1.55 (2)	C(204)–C(205)	1.36 (2)	C(404)–C(405)	1.33 (2)
C(114)–C(115)	1.54 (2)	C(214)–C(215)	1.52 (2)	–C(207)	1.53 (2)	–C(407)	1.64 (3)
C(114)–C(116)	1.54 (2)	C(214)–C(216)	1.58 (2)	C(205)–C(206)	1.47 (2)	C(405)–C(406)	1.50 (2)
C(121)–C(122)	1.51 (2)	C(221)–C(222)	1.54 (1)	C(301)–C(302)	1.43 (2)	C(501)–C(502)	1.55 (2)
C(122)–C(123)	1.61 (2)	C(222)–C(223)	1.57 (2)	–C(306)	1.40 (2)	–C(506)	1.32 (2)
C(122)–N(121)	1.45 (2)	C(222)–N(221)	1.47 (1)	C(302)–C(303)	1.39 (3)	C(502)–C(503)	1.41 (3)
C(123)–C(124)	1.54 (2)	C(223)–C(224)	1.58 (2)	C(303)–C(304)	1.40 (3)	C(503)–C(504)	1.46 (2)
C(124)–C(125)	1.51 (2)	C(224)–C(225)	1.56 (3)	C(304)–C(305)	1.34 (2)	C(504)–C(505)	1.42 (2)
C(124)–C(126)	1.53 (2)	C(224)–C(226)	1.57 (2)	–C(307)	1.60 (2)	–C(507)	1.63 (3)
C(131)–C(132)	1.52 (1)	C(231)–C(232)	1.54 (1)	C(305)–C(306)	1.53 (2)	C(505)–C(506)	1.33 (2)

B. Bond Angles

Mo(2)–Mo(1)–O(11)	91.2 (2)	Mo(4)–Mo(3)–O(31)	92.1 (2)
–O(12)	92.4 (2)	–O(32)	90.9 (2)
–O(13)	91.7 (2)	–O(33)	91.4 (2)
–O(14)	90.5 (2)	–O(34)	89.9 (2)
–Cl(1)	173.00 (6)	–Cl(3)	171.93 (6)
Mo(1)–Mo(2)–O(21)	91.6 (2)	Mo(3)–Mo(4)–O(41)	91.1 (2)
–O(22)	90.4 (2)	–O(42)	92.6 (2)
–O(23)	91.8 (2)	–O(43)	91.2 (2)
–O(24)	91.8 (2)	–O(44)	93.5 (2)
–O(303)	153.7 (2)	–O(202)	176.8 (2)
–O(302)	159.8 (2)	–O(201)	136.7 (2)
O(11)–Mo(1)–O(12)	88.2 (3)	O(31)–Mo(3)–O(32)	176.8 (3)
–O(13)	89.4 (3)	–O(33)	89.1 (2)
–O(14)	178.3 (3)	–O(34)	90.3 (3)
–Cl(1)	95.5 (2)	–Cl(3)	90.1 (2)
O(12)–Mo(1)–O(13)	175.4 (3)	O(32)–Mo(3)–O(33)	89.6 (2)
–O(14)	92.1 (3)	–O(34)	90.9 (2)
–Cl(1)	89.9 (2)	–Cl(3)	87.1 (2)
O(13)–Mo(1)–O(14)	90.2 (3)	O(33)–Mo(3)–O(34)	178.7 (3)
–Cl(1)	86.4 (2)	–Cl(3)	96.4 (2)
O(14)–Mo(1)–Cl(1)	87.8 (2)	O(34)–Mo(3)–Cl(3)	82.4 (2)
C(21)–Mo(2)–O(22)	90.3 (3)	O(41)–Mo(4)–O(42)	176.1 (2)
–O(23)	89.6 (3)	–O(43)	91.2 (3)
–O(24)	176.1 (3)	–O(44)	89.6 (3)
–O(303)	76.4 (3)	–O(202)	86.5 (3)
–O(302)	101.0 (3)	–O(201)	55.8 (3)
O(22)–Mo(2)–O(23)	177.9 (3)	O(42)–Mo(4)–O(43)	90.1 (3)
–O(24)	91.7 (3)	–O(44)	88.8 (3)
–O(303)	66.8 (3)	–O(202)	89.9 (3)
–O(302)	105.2 (3)	–O(201)	121.6 (3)
O(23)–Mo(2)–O(24)	88.2 (3)	O(43)–Mo(4)–O(44)	175.2 (3)
–O(303)	111.1 (3)	–O(202)	86.7 (3)
–O(302)	72.7 (2)	–O(201)	65.5 (3)
O(303)–Mo(2)–O(302)	46.3 (3)	O(202)–Mo(4)–O(201)	40.1 (3)
Mo(1)–O(11)–C(111)	118.1 (6)	Mo(3)–O(31)–C(211)	113.9 (6)
Mo(1)–O(12)–C(121)	117.3 (7)	Mo(3)–O(32)–C(221)	117.0 (6)
Mo(1)–O(13)–C(131)	116.3 (6)	Mo(3)–O(33)–C(231)	116.1 (5)
Mo(1)–O(14)–C(141)	118.3 (6)	Mo(3)–O(34)–C(241)	115.8 (7)
Mo(2)–O(21)–C(111)	115.8 (6)	Mo(4)–O(41)–C(211)	115.4 (6)
Mo(2)–O(22)–C(121)	117.5 (6)	Mo(4)–O(42)–C(221)	113.8 (6)
Mo(2)–O(23)–C(131)	116.3 (6)	Mo(4)–O(43)–C(231)	116.9 (6)
Mo(2)–O(24)–C(141)	117.4 (6)	Mo(4)–O(44)–C(241)	116.4 (6)

Table II (*Continued*)

O(11)-C(111)-O(21)	123.4 (9)	O(31)-C(211)-O(41)	127 (1)
O(11)-C(111)-C(112)	122.1 (9)	O(31)-C(211)-C(212)	113.8 (9)
O(21)-C(111)-C(112)	114.6 (9)	O(41)-C(211)-C(212)	118.7 (9)
C(111)-C(112)-C(113)	111.0 (9)	C(211)-C(212)-C(213)	113.3 (9)
C(111)-C(112)-N(111)	107.5 (9)	C(211)-C(212)-N(211)	105.7 (9)
C(113)-C(112)-N(111)	112.0 (9)	C(213)-C(212)-N(211)	109.5 (9)
C(112)-C(113)-C(114)	114.3 (9)	C(212)-C(213)-C(214)	115 (1)
C(113)-C(114)-C(115)	108 (1)	C(213)-C(214)-C(215)	107 (1)
C(113)-C(114)-C(116)	115 (1)	C(213)-C(214)-C(216)	112 (1)
C(115)-C(114)-C(116)	110 (1)	C(215)-C(214)-C(216)	112 (1)
O(12)-C(121)-O(22)	122 (1)	O(32)-C(221)-O(42)	125.6 (9)
O(22)-C(121)-C(122)	119 (1)	O(32)-C(221)-C(222)	118.4 (9)
O(22)-C(121)-C(122)	117.7 (9)	O(42)-C(221)-C(222)	116.0 (9)
C(121)-C(122)-C(123)	107.5 (9)	C(221)-C(222)-C(223)	112.1 (9)
C(121)-C(122)-N(121)	110 (1)	C(221)-C(222)-N(221)	107.9 (8)
C(122)-C(123)-N(121)	106.0 (9)	C(223)-C(222)-N(221)	108.3 (8)
C(123)-C(123)-C(124)	116 (1)	C(222)-C(223)-C(224)	109 (1)
C(123)-C(124)-C(125)	108 (1)	C(223)-C(224)-C(225)	107 (1)
C(123)-C(124)-C(126)	112 (1)	C(223)-C(224)-C(226)	111 (1)
C(125)-C(124)-C(126)	113 (1)	C(225)-C(224)-C(226)	110 (1)
O(13)-C(131)-O(23)	124.0 (9)	O(33)-C(231)-O(43)	124.5 (8)
O(13)-C(131)-C(132)	118.4 (9)	O(33)-C(231)-C(232)	120.4 (8)
O(23)-C(131)-C(132)	117.6 (9)	O(43)-C(231)-C(232)	115.1 (8)
C(131)-C(132)-C(133)	114.3 (9)	C(231)-C(232)-C(233)	110.1 (8)
C(131)-C(132)-N(131)	105.8 (8)	C(231)-C(232)-N(231)	108.2 (8)
C(133)-C(132)-N(131)	110.5 (9)	C(233)-C(232)-N(231)	111.7 (8)
C(132)-C(133)-C(134)	113 (1)	C(232)-C(233)-C(234)	113.1 (9)
C(133)-C(134)-C(135)	109 (1)	C(233)-C(234)-C(235)	108 (1)
C(133)-C(134)-C(136)	111 (1)	C(233)-C(234)-C(236)	113 (1)
C(135)-C(134)-C(136)	112 (1)	C(235)-C(234)-C(236)	111 (1)
O(14)-C(141)-O(24)	121.9 (9)	O(34)-C(241)-O(44)	124.3 (9)
O(14)-C(141)-C(142)	120.4 (9)	O(34)-C(241)-C(242)	117.2 (9)
O(24)-C(141)-C(142)	117.5 (9)	O(44)-C(241)-C(242)	118.5 (9)
C(141)-C(142)-C(143)	115.8 (9)	C(241)-C(242)-C(243)	116.2 (9)
C(141)-C(142)-N(141)	107.0 (9)	C(241)-C(242)-N(241)	104.7 (8)
C(143)-C(142)-N(141)	107.8 (8)	C(243)-C(242)-N(241)	110.5 (9)
C(142)-C(143)-C(144)	113.6 (9)	C(242)-C(243)-C(244)	113 (1)
C(143)-C(144)-C(145)	108 (1)	C(243)-C(244)-C(245)	104 (1)
C(143)-C(144)-C(146)	107 (1)	C(243)-C(244)-C(246)	115 (2)
C(145)-C(144)-C(146)	109 (2)	C(245)-C(244)-C(246)	106 (2)
O(201)-S(20)-O(202)	112.0 (5)	O(401)-S(40)-O(402)	110.9 (6)
-O(203)	112.6 (5)	-O(403)	114.6 (6)
-C(201)	105.5 (5)	-C(401)	104.8 (6)
O(202)-S(20)-O(203)	111.3 (4)	O(402)-S(40)-O(403)	113.4 (6)
-C(201)	108.0 (5)	-C(401)	104.9 (6)
O(203)-S(20)-C(201)	107.1 (5)	O(403)-S(40)-C(401)	107.4 (6)
O(301)-S(30)-O(302)	110.7 (5)	O(501)-S(50)-O(502)	114.7 (7)
-O(303)	110.5 (5)	-O(503)	106.3 (7)
-C(301)	107.2 (5)	-C(501)	102.9 (8)
O(302)-S(30)-O(303)	114.4 (6)	O(502)-S(50)-O(503)	114.6 (7)
-C(301)	108.6 (6)	-C(501)	109.1 (7)
O(303)-S(30)-C(301)	105.1 (6)	O(503)-S(50)-C(501)	108.5 (7)
S(20)-C(201)-C(202)	120.8 (9)	S(40)-C(401)-C(402)	123 (1)
S(20)-C(201)-C(206)	117 (1)	S(40)-C(401)-C(406)	114 (1)
C(202)-C(201)-C(206)	122 (1)	C(402)-C(401)-C(406)	123 (1)
C(201)-C(202)-C(203)	120 (1)	C(401)-C(402)-C(403)	122 (1)
C(202)-C(203)-C(204)	119 (1)	C(402)-C(403)-C(404)	115 (1)
C(203)-C(204)-C(205)	120 (2)	C(403)-C(404)-C(405)	127 (2)
C(203)-C(204)-C(207)	119 (2)	C(403)-C(404)-C(407)	118 (2)
C(205)-C(204)-C(207)	121 (1)	C(405)-C(404)-C(407)	115 (2)
C(204)-C(205)-C(206)	121 (2)	C(404)-C(405)-C(406)	119 (2)
C(201)-C(206)-C(205)	118 (1)	C(401)-C(406)-C(405)	113 (1)
S(30)-C(301)-C(302)	118 (1)	S(50)-C(501)-C(502)	113 (1)
S(30)-C(301)-C(306)	117 (1)	S(50)-C(501)-C(506)	124 (1)
C(302)-C(301)-C(306)	125 (1)	C(502)-C(501)-C(506)	122 (2)
C(301)-C(302)-C(303)	118 (2)	C(501)-C(502)-C(503)	113 (2)
C(302)-C(303)-C(304)	121 (2)	C(502)-C(503)-C(504)	123 (2)
C(303)-C(304)-C(305)	122 (2)	C(503)-C(504)-C(505)	117 (2)
C(303)-C(304)-C(307)	119 (2)	C(503)-C(504)-C(507)	121 (2)
C(305)-C(304)-C(307)	118 (2)	C(505)-C(504)-C(507)	122 (2)
C(304)-C(305)-C(306)	121 (2)	C(504)-C(505)-C(506)	123 (2)
C(301)-C(306)-C(305)	113 (1)	C(501)-C(506)-C(505)	123 (2)

circular activity is permitted, and this might distort the crystal spectra.[12] Fortunately, these difficulties did not manifest themselves to any detectable extent. All peaks maximized or minimized at the same polarizer angle settings. A further source of potential complications was the presence of two crystallographically independent molecules. However, as

---

[12] Royer, D. J. *Inorg. Chem.* **1978**, *17*, 513.

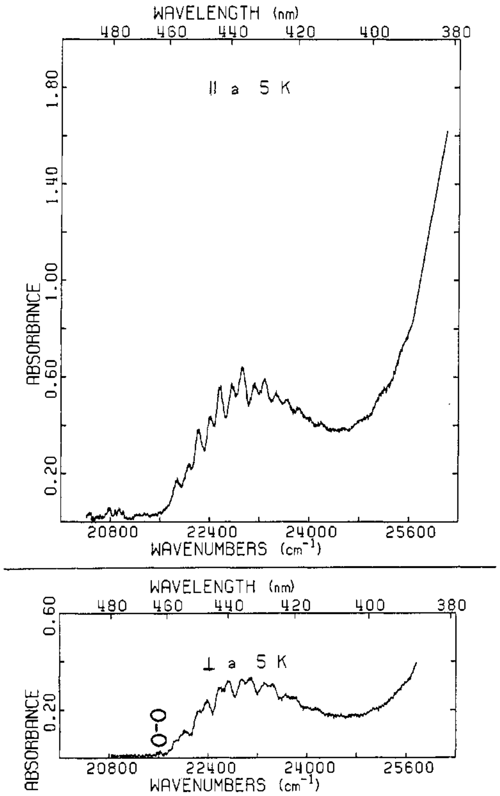

Figure 3. Observed polarized spectra at 5 K recorded in the 010 crystal face, || and ⊥ to the crystallographic *a* axis.

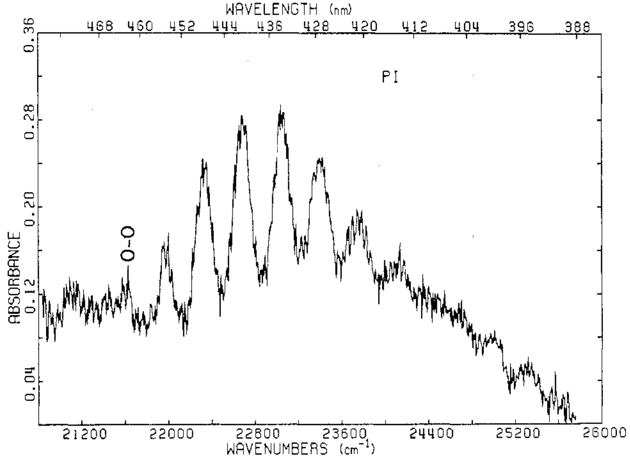

Figure 4. Spectrum polarized parallel to the molecular axis: the *z*-polarized or π spectrum.

already noted, the metal–metal vectors for these two molecules are almost perfectly parallel. For parallel vectors one of the potential Davidov states vanishes (assuming idealized D_{4h} symmetry). The result of the fortuitous parallel arrangement, then, is that this system can be treated as if there were only one independent molecule in the cell.

The alignment of the molecules in the tetraglycine complex was such that experimental measurements provided directly the spectra polarized parallel and perpendicular to the molecular fourfold axis. In the present case that does not happen because of the oblique orientations of the $[Mo_2(L\text{-leucine})_4]^{4+}$ ions. However, we have been able to obtain the molecularly polarized spectra by using the method of Piper.[13] The observed spectra, stored in digital form in the computer as an intensity value every 0.2 nm, were resolved and replotted as spectra polarized parallel to and perpendicular to the molecular axis. This was accomplished with the use of locally written software with "Piper" angles of θ = 137.50° and φ = 78.82° obtained from the crystal structure. The results are shown in Figures 4 and 5 for the parallel (π) and perpendicular (σ) polarizations, respectively.

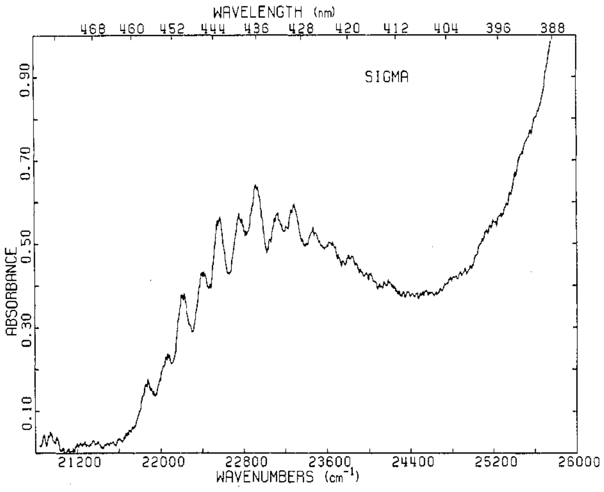

Figure 5. Spectrum polarized perpendicular to the molecular axis: the *xy*-polarized or σ spectrum.

Table III. Vibrational Components

λ	ν, cm^{-1} *z*	*xy*	*xy*	$\Delta\nu$, cm^{-1}	comments
463.1	21 594				0–0 band
457.7		21 851			256 ± 2 cm^{-1} above 0–0
455.6	21 949			356	
453.8			22 036		445 ± 7 cm^{-1} above 0–0
450.3		22 207		357	
448.4	22 302			353	
446.6			22 391	355	
443.3		22 558		351	
441.5	22 650			348	
439.8			22 738	347	
436.6		22 904		346	
434.8	22 999			349	
433.0			23 095	357	
430.0		23 256		352	
428.3	23 348			349	
426.6			23 441	346	
423.7		23 602		346	
422.1	23 691			343	mean $\Delta\nu$ = 347 ± 5 cm^{-1}
420.2			23 798	357	
417.6		23 946		344	
416.3	24 021			330	
414.1			24 149	351	

It is evident that there is a clean separation into *z* and *xy* polarizations, which shows that in this case, just as in the case of the glycine complex, the oriented gas model is valid within the accuracy and sensitivity of the measurements.

The resulting molecular spectra for the tetraleucine dimer are very similar to those observed for the tetraglycine dimer. The only important difference is the absence of the first, weak, *z*-polarized progression. Several thicker crystals of the tetraleucine compound were studied, and in no case was any absorption observed at energies lower than the 0–0 band at 21 594 cm^{-1}. The frequencies of the maxima in Figures 4 and 5 are listed in Table III. In all other respects the spectrum is quite comparable to that of the tetraglycine compound. The origin in $[Mo_2(O_2CCH_2NH_3)_4]^{4+}$ at 21 510 cm^{-1} is within 90 cm^{-1} of the one observed here. The two *xy* progressions begin at 256 ± 2 and 445 ± 7 cm^{-1} above the 0–0 line in the tetraleucine complex; the corresponding shifts are 261 ± 12 and 400 ± 13 cm^{-1} for the tetraglycine complex. The average

---

(13) Piper, T. S. *J. Chem. Phys.* **1961**, *35*, 1240.

separation for the progressions was 344 ± 10 cm^{-1} for the tetraglycine complex and 347 ± 5 cm^{-1} for the leucine complex. Again only this one value is observed for all progressions.

It is interesting that for both of the tetrakis(amino acid) complexes studied the oriented gas polarization ratios are strictly satisfied while for the tetracarboxylic acid compounds they are not. The only obvious difference between these two classes of compound is that the amino acid complexes are 4+ ions with charges on the periphery because of the zwitterionic nature of the amino acids, while the tetracarboxylates crystallize as a van der Waals packing of neutral molecules. The ionic nature of the former type of crystal could lead to the observed accurate alignment of the transition moments for two reasons. First, the presence of intervening anions causes the intermolecular distances to be larger, and this should result in less intermolecular borrowing of intensity. It is this borrowing that causes a shift of the transition moment from that of the molecular axes. Second, the highly anisotropic field created by the charge distribution in the ionic crystal may force the transition moment to align with the molecular axes.

Conclusions. The spectral results of the present study are in remarkably close agreement with those obtained for $[Mo_2(O_2CCH_2NH_3)_4](SO_4)_2 \cdot 4H_2O$, except that the low-energy, weak progression in *z* polarization is absent. We feel that this affords a strong indication that this progression is spurious and probably, as suggested by Martin, Newman, and Fanwick,[6] originates in an impurity. The three progressions that are genuinely due to the $[Mo_2(O_2CCRNH_3)_4]^{4+}$ ions in each case can then be fully reconciled with the $\delta^* \leftarrow \delta$ assignment, exactly as shown by Martin, Newman, and Fanwick in the case of $Mo_2(O_2CCH_3)_4$.

Acknowledgment. We are grateful to the National Science Foundation for support of this research, including funds for the building of the spectrometer.

Registry No. Mo_2(L-leucine)$_4Cl_2$(pts)$_2 \cdot 2H_2O$, 72845-27-3; $K_4Mo_2Cl_8$, 25448-39-9.

Supplementary Material Available: A table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of North Dakota, Grand Forks, North Dakota 58202

Crystal and Molecular Structures of π-Toluene Complexes of $(C_6F_5)_2Co$ and $(C_6F_5)_2Ni$

L. J. RADONOVICH,* K. J. KLABUNDE,* C. B. BEHRENS, D. P. McCOLLOR, and B. B. ANDERSON

Received August 28, 1979

$(\pi\text{-}C_6H_5CH_3)Co(C_6F_5)_2$ and $(\pi\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$ crystallize in space group *Pnma* with four molecules per unit cell. The structures were determined from 1335 and 1741 observed diffractometer data and refined to *R* values of 6.1 and 5.2% for the cobalt and nickel compounds, respectively. The structures consist of the metal atoms σ bonded to two C_6F_5 groups and π bonded to one toluene ligand in an arrangement of *m*(*Cs*) symmetry which is fully utilized crystallographically. Relatively short M–C σ bonds of 1.931 (5) Å for the cobalt compound and 1.891 (4) Å for the nickel compound are observed while the M–ring distances are 1.627 Å (Co) and 1.681 Å (Ni). The longer π bonds in the nickel compound suggest that the additional electron ($\text{Co} \rightarrow \text{Ni}$) resides in an orbital that is antibonding with respect to the arene ligand. The toluene ligand is planar in the cobalt complex but a small "boat" type distortion amounting to a rotation of the two end carbons of ~4° away from the metal is observed in the nickel complex.

Introduction

Examples of π-arene complexes of the group 8 metals include M(0),[1] M(I),[2] M(II),[3] and M(III)[4] species.[5] In recent years these complexes have attracted a good deal of interest for a variety of reasons including their catalytic properties[6] and, in particular, the observation that the π-arene ligand can be extremely labile in solution.[7,8] This lability is of fundamental importance since the dissociation of a π-arene ligand generates three possible coordination sites.

Because of the new synthetic procedures available to us and the limited extent of structural data available in general on π-arene complexes, we have established a vigorous program to characterize structurally a series of cobalt(II) and nickel(II) complexes. Previously, we have reported the synthesis of the first example of an R_2M–π-arene complex,[9] $(C_6F_5)_2Co$–π-toluene, and the preliminary results of an X-ray structure determination. More recently, we have reported the synthesis and some of the interesting chemistry of the analogous nickel(II) compound.[8] Herein, we report the complete results of the structure determination of the paramagnetic $(C_6F_5)_2Co$–π-toluene complex and also the results of a structure deter-

---

(1) (a) Fischer, E. O.; Rohrscheid, F. *Z. Naturforsch., B* **1962**, *17*, 483. (b) Weber, S. R.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 45. (c) Timms, P. L. *Chem. Commun.* **1969**, 1033. (d) Klabunde, K. J.; Efner, H. F.; Murdock, T. O.; Ropple, R. *J. Am. Chem. Soc.* **1976**, *98*, 1021. (e) Middleton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 120. (f) Williams-Smith, D. L.; Wolf, L. R.; Skell, P. S. *J. Am. Chem. Soc.* **1972**, *94*, 4042. (g) Meuller, J.; Kreiter, C. G.; Mertschenk, B.; Schmitt, S. *Chem. Ber.* **1975**, *108*, 273. (h) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A.; *J. Organomet. Chem.* **1976**, *121*, C18. (i) Werner, H.; Werner, R. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 683.

(2) (a) Tsutsui, M.; Zeiss, H. H. *Naturwissenschaften* **1957**, *44*, 420. (b) Khand, I. V., Pauson, P. L.; Watts, W. E., *J. Chem. Soc., C* **1969**, 2024. (c) Tsutsui, M.; Zeiss, H. *J. Am. Chem. Soc.* **1961**, *83*, 825. (d) Fischer, E. O.; Fischer, R. D. *Z. Naturforsch., B* **1961**, *16*, 556. (e) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

(3) (a) Fischer, E. O.; Elschenbroich, C. *Chem. Ber.* **1970**, *103*, 162. (b) Fischer, E. O.; Böttcher, R. *Chem. Ber.* **1956**, 2397. Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7207. (c) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063. (d) Zelonka, R. A.; Baird, M. C. *J. Organomet. Chem.* **1972**, *44*, 383. (e) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233. (f) Winkhaus, G.; Singer, H. *J. Organomet. Chem.* **1967**, *7*, 487. (g) Ogata, I.; Irvata, R.; Ikeda, Y. *Tetrahedron Lett.* **1970**, 3011. (h) Taraone, F.; Marsala, V. *Inorg. Chim. Acta* **1978**, *27*, L109.

(4) (a) White, C.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 3322. (b) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654. (c) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (d) Booth, B. L.; Hazeldine, R. N.; Hill, M. *Chem. Commun.* **1967**, 1118.

(5) Gastinger, R. G.; Klabunde, K. J. *Transition Met. Chem.*, in press (a review of π-arene–group 8 complexes).

(6) (a) Johnson, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7395. (b) Ogata, I.; Irvata, R.; Ikeda, Y. *Tetrahedron Lett.* **1970**, 3011. (c) Hinze, A. G. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 542.

(7) Green, M.; Kuc, T. A. *J. Chem. Soc., Dalton Trans.* **1972**, 832.

(8) Klabunde, K. J.; Anderson, B. B.; Bader, M.; Radonovich, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1313.

(9) Anderson, B. B.; Behrens, C.; Radonovich, L. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1976**, *98*, 5390.

0020-1669/80/1319-1221$01.00/0
© 1980 American Chemical Society