Vanadium(III)–α-Amino Acid Homoleptic Complexes from Non-Protic Solutions: Reactions of [V(Mes)$_3$(THF)] with α-Amino Acids and the Structures of Tris(L-prolinato)vanadium–Dimethyl Sulfoxide and Tris(D-prolinato)vanadium–Dimethyl Sulfoxide

C. Philippe Magill,† Carlo Floriani,*,† Angiola Chiesi-Villa,‡ and Corrado Rizzoli‡

Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland, and Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy

Received December 8, 1992

The reaction of [V(Mes)$_3$(THF)] [Mes ≡ 2,4,6-Me$_3$C$_6$H$_2$] with free α-amino acids in non-protic solvents led to the synthesis of homoleptic mononuclear hexacoordinate vanadium(III) complexes VA$_3$ [AH = L-proline, **1**; AH = D-proline, **2**; AH = L-phenylalanine, **3**; AH = D-phenylalanine, **4**; AH = D,L-phenylalanine, **5**; AH = L-tryptophan, **6**; AH = L-valine, **7**]. The solubility of the products varies according to the nature of the amino acid. The crystalline solids contain solvents of crystallization. The structures of **1**·DMSO and **2**·DMSO have been elucidated by an X-ray analysis. The configuration of **1** corresponds to the *mer* Δ diastereoisomeric form which is one of the four possible distereoisomers of the tris(L-prolinato)vanadium complex, while the configuration of **2** is the *mer* Λ form which is one of the four diastereoisomers of tris(D-prolinato)vanadium(III). The optical rotations of all complexes are very high when compared with those for uncomplexed α-amino acids ($[\alpha]_D^{20}$ = 312° for **1** *vs* –85.0° for L-proline; –318° for **2** *vs* +81.5° for D-proline), the sign of the rotation for **1** being opposite to that seen for complexes **3**, **6**, and **7**. Crystallographic details: **1** is monoclinic, space group $P2_1$, a = 10.468(9) Å, b = 19.125(6) Å, c = 11.448(4) Å, $\alpha = \gamma = 90°$, β = 109.27(4)°, Z = 4, R = 0.043; **2** is monoclinic, space group $P2_1$, a = 10.486(2) Å b = 19.130(3) Å, c = 11.470(2) Å, $\alpha = \gamma = 90°$, β = 109.31(2)°, Z = 4, R = 0.040.

Introduction

The biochemistry of vanadium is a topic of current interest.[1] Attention has been focused on the accumulation of the metal in tunicates,[2] and in a mushroom from which the natural product amavanadin has been isolated.[3] Notable also is the discovery of a vanadium-containing nitrogenase[4] and a vanadate-dependent haloperoxidase.[5] The capacity of reduced forms of vanadium to fix nitrogen has been well documented.[6] The biological effects of the metal include the stimulation of plant and algae growth,[7] and the inhibition of Na,K-ATPase.[8] Also, vanadium is thought to play a role in glucose metabolism,[9] and in renal and bladder function.[10]

In spite of all of these biological implications, little is known concerning the interaction of vanadium with α-amino acids[11] as compared with other first row transition metals.[12] Studies have been done using spectroscopic techniques on vanadate (V(V)), vanadyl (V(IV))[13] and V(III)[14] amino acid complexes in aqueous solution, however no complexes have been structurally characterized. This is an area that deserves more attention in view of the potential use of these compounds as models for vanadium-binding sites in metalloproteins.

It has been noted that actual metal-binding in metalloproteins takes place under de facto non-aqueous conditions since active sites frequently lie in clefts or pockets in the protein structure which are lined with predominantly nonpolar amino acid side-chains.[15] With this in mind, we have undertaken a new approach, namely the preparation of transition metal–amino acid complexes in non-aqueous media. These can be regarded as building blocks for making chiral metal aggregates. We herein describe the preparation in THF solution of a series of tris(amino acidato)-vanadium(III) complexes and report the crystal structures of two of these, tris(L-prolinato)vanadium–dimethyl sulfoxide and tris(D-prolinato)vanadium–dimethyl sulfoxide.

* To whom correspondence and reprint requests should be addressed.
† University of Lausanne.
‡ University of Parma.

(1) Butler, A.; Carrano, C. J. *Coord. Chem. Rev.* **1991**, *109*, 61.
(2) (a) Kustin, K; McCara, I. C. *Struct. Bonding (Berlin)* **1983**, *53*, 139 and references therein. (b) Kustin, K; McCara, I. C. *Comments Inorg. Chem.* **1982**, *2*, 1 and references therein. (c) Smith, M. J. *Experientia* **1989**, *45*, 452 and references therein.
(3) (a) Bayer, E.; Kneifel, H. *Z. Naturforsch.* **1972**, *27B*, 20. (b) Kneifel, H.; Bayer, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508. (c) Kneifel, H.; Bayer, E. *J. Am. Chem. Soc.* **1986**, *108*, 3075. (d) Corrondo, M. A. A. F. de C. T.; Duarte, M. T. L. S.; Costa Pessoa, J.; Silva, J. A. L.; Fraústo da Silva, J. J. R.; Vaz, M. C. T. A.; Vilas-Boas, L. F. *J. Chem. Soc., Chem. Commun.* **1988**, 1158.
(4) (a) Hales, B. J.; Case, E. E.; Morningstar, J. E.; Dzeda, M. F.; Mauterer, L. A. *Biochemistry* **1986**, *25*, 7251. (b) Robson, R. L.; Eady, R. R.; Richardson, T. H.; Miller, R. W.; Hawkins, M.; Postgate, J. R. *Nature (London)* **1986**, *322*, 388. (c) Arber, J. M.; Dobson, B. R.; Eady, R. R.; Stevens, P.; Hasnain, S. S.; Garner, C. D.; Smith, B. E. *Nature (London)* **1986**, *325*, 372.
(5) (a) Vilter, H. *Phytochemistry* **1984**, *23*, 1387. (b) de Boer, E.; van Kooyk, Y.; Tromp, M. G. M.; Plat, H.; Wever, R. *Biochim. Biophys. Acta* **1986**, *869*, 48. (c) Krenn, B. E.; Plat, H.; Wever, R. *Biochim. Biophys. Acta* **1987**, *912*, 287. (d) Plat, H.; Krenn, B. E.; Wever, R. *Biochem. J.* **1987**, *248*, 277.
(6) Shilov, A. E. *Perspectives in Coordination Chemistry*; Verlag Helvetica Chemica Acta: Basel, 1992; and references therein.
(7) Meisch, H.-U.; Bieleg, H.-J. *Basic Res. Cardiol.* **1980**, *75*, 413.
(8) Cantley, L. C., Jr.; Josephson, L.; Warner, R.; Yanagisawa, M.; Lechene, C.; Guidotti, G. *J. Biol. Chem.* **1977**, *252*, 7421.
(9) Crans, D. C.; Wilging, E. M.; Butler, S. R. *J. Am. Chem. Soc.* **1990**, *112*, 427.
(10) Holloway, C. E.; Melnick, M. *Rev. Inorg. Chem.* **1985**, *7*, 75 and references therein.
(11) Boas, V. L.; Pessoa, J. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 3; Chapter 33, p 484.
(12) Laurie, S. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 2; Chapter 20.2.
(13) (a) Theriot, L. J.; Carlisle, G. O.; Hu, H. J. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2841. (b) Syamal, A.; Theriot, L. J. *J. Coord. Chem.* **1973**, *2*, 193. (c) Casella, L.; Gullotti, M.; Pintar, A.; Colonna, S.; Manfredi, A. *Inorg. Chim. Acta* **1988**, *144*, 89. (d) Costa Pessoa, J.; Vilas Boas, L. F.; Gillard, R. D.; Lancashire, R. J. *Polyhedron* **1988**, *7*, 1245. (e) Crans, D. C.; Bunch, R. L.; Thiesen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 7597. (f) Rehder, D. *Inorg. Chem.* **1988**, *27*, 4312.
(14) (a) Kovala-Demertzi, D; Demertzis, M; Tsangaris, J. M. *Bull. Soc. Chim. Fr.* **1986**, *4*, 558. (b) Kovala-Demertzi, D; Demertzis, M; Tsangaris, J. M. *Bull. Soc. Chim. Fr.* **1988**, *5*, 793.
(15) Freeman, H. C. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. 1.

0020-1669/93/1332-2729$04.00/0

Table I. Summary of Results

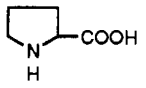
compound			anal. found, %			anal. calcd, %					
no.	formula	yield, %	C	H	N	C	H	N	$[\alpha]_D^{20}$, deg	μ_{eff}, μ_B	ν(CO), cm^{-1}
1	V(L-PRO)$_3$·DMSO	58	43.51	6.71	8.66	43.31	6.41	8.91	+312[a]	2.58	1636
2	V(D-PRO)$_3$·DMSO	55	43.06	6.73	8.72	43.31	6.41	8.91	−318[a]	2.62	1634
3	V(L-PHE)$_3$·THF	65	60.94	5.96	6.42	60.48	6.22	6.83	−276[b]	2.61	1651
4	V(D-PHE)$_3$·THF	66	59.81	5.90	7.65	60.48	6.22	6.83	+272[b]	2.67	1651
5	V(DL-PHE)$_3$·THF	50	58.88	6.00	6.00	60.48	6.22	6.83	0[b]	3.09	1581
6	V(L-TRP)$_3$·THF	61	60.53	5.70	11.57	60.65	5.64	11.47	−148[b]	2.55	1645
7	V(L-VAL)$_3$·2DMSO	25	41.31	7.86	7.74	41.07	7.62	7.56	−158[a]	2.73	1643

[a] C = 1 in DMSO. [b] C = 1 in THF.

Results and Discussion

Trimesitylvanadium(III), [V(Mes)$_3$(THF)] [Mes ≡ 2,4,6-Me$_3$C$_6$H$_2$] was chosen as the starting material for this work since it is easily prepared and can react readily with protic sources such as α-amino acids, AH, to form VA$_3$ complexes by liberating mesitylene:

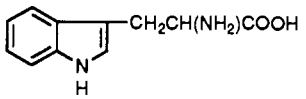
$$[V(Mes)_3(THF)] + 3\,AH \xrightarrow{THF} [V(A)_3] + 3MesH \quad (1)$$



AH = L-proline (1)
AH = D-proline (2)

$PhCH_2CH(NH_2)COOH$

AH = L-phenylalanine (3)
AH = D-phenylalanine (4)
AH = DL-phenylalanine (5)



AH = L-tryptophan (6)

$Me_2CHCH(NH_2)COOH$

AH = L-valine (7)

The main problem was in finding α-amino acids that had some discernible solubility in aprotic organic solvents. In this regard, proline, phenylalanine, and tryptophan proved to be suitable and these reacted slowly with [V(Mes)$_3$(THF)] in THF solution at room temperature to give the desired tris(amino acidato)vanadium(III) complexes. In the case of valine, the addition of a pinch of LiCl was necessary for the reaction to proceed.[16] The results of these reactions are summarized in Table I.

The solubilities of the products varied according to the size of the amino acid substituents. Bulky substituents change the geometry and reduce the strength of the hydrogen-bond network. Solubilization and recrystallization of complexes **1**–**7** from polar solvents leads to the isolation of the corresponding solvated forms. The major role of the solvent is, very probably, to break down a polymeric form derived from strong hydrogen bond interactions, by way of the solvent remaining hydrogen-bonded in the structure, as shown in the structures of the solvated forms of **1** and **2** in Figure 4. Thus complexes **3**–**5** could be recrystallized from THF/Et$_2$O solutions while the prolinato **1** and **2** and valinato **7** complexes were only soluble in DMSO. The solvated forms of complexes **1**, **2**, and **7** contain one [**1** and **2**] or two [**7**] molecules of DMSO, while **4**–**6** contain a single molecule of THF. By layering DMSO solutions of V(L-Pro)$_3$·DMSO, **1**·DMSO, and V(D-Pro)$_3$·DMSO, **2**·DMSO, with ether and allowing the solvents to diffuse slowly over several days, we obtained crystals suitable for X-ray analysis. The structures of complexes **1** and **2** are shown in Figures 1 and 2 and selected structural parameters are given in Table V.

The structure of complex **1** consists of the packing of tris(L-prolinato)vanadium complex molecules and DMSO solvent molecules in the stoichiometric molar ratio 1/1. In the asymmetric unit cell, there are two independent molecules (called A and B) having similar geometries. In each complex molecule, the three prolinato residues form chelate rings at the metal atom through their nitrogen atoms and one oxygen atom so as to give a slightly distorted octahedral coordination. The configuration of the complex, unambiguously determined by X-ray analysis, corresponds to the *mer* Δ diasteriomeric form which is one of the four possible diasteriomers for the tris(L-prolinato)vanadium complex (Figure 5). The structure of complex **1** is comparable with those of tris(glycinato)cobalt(III) dihydrate,[17] tris(L-alaninato)cobalt(III) monohydrate,[18] and tris(β-alaninato)cobalt(III) tetrahydrate,[19] which all adopt a *mer* Δ configuration. Tris(glycinato)chromium(III) monohydrate adopts a facial diasteriomeric form.[20]

Table II. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds **1**, **2**

	1	**2**
chem formula	$C_{15}H_{24}N_3O_6V\cdot C_2H_6SO$	$C_{15}H_{24}N_3O_6V\cdot C_2H_6SO$
a, Å	10.468(9)	10.486(2)
b, Å	19.125(6)	19.130(3)
c, Å	11.448(4)	11.470(2)
α, deg	90	90
β, deg	109.27(4)	109.31(2)
γ, deg	90	90
V Å^3	2164(2)	2171.4(7)
Z	4	4
fw	471.4	471.4
space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)
T, °C	22	22
λ, Å	0.710 69	1.541 78
ρ_{calc}, g cm^{-3}	1.447	1.442
μ, cm^{-1}	5.76	51.13
transm coeff	0.799–1.000	0.692–1.000
R[a]	0.043	0.040
R_w	0.047	0.044
R_G	0.059	0.055

[a] $R = \Sigma|\Delta F|/\Sigma|F_o|$. $R_w = [\Sigma w^{1/2}|\Delta F|/\Sigma w^{1/2}|F_o|]$. $R_G = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{1/2}$.

The vanadium–oxygen and vanadium–nitrogen bond distances are in the range found in vanadium(III)–Schiff base complexes.[21] The small, even if significant, differences observed within the V–O and V–N distances could be related to intraligand steric interactions. The five-membered chelate rings are distorted from planarity and show significant puckering differences. They assume envelope conformations as can be seen from the values quoted in Table V.

(16) Seebach showed that the addition of inorganic salts such as LiCl greatly enhances the solubility of peptides in nonpolar solvents. We found that this is also true for α-amino acids: Seebach, D.; Thaler, A.; Beck, A. K. *Helv. Chim. Acta* **1989**, *72*, 857.

(17) (a) Miyanaga, A.; Sakaguchi, U; Morimoto, Y; Kushi, Y; Yoneda, H *Inorg. Chem.* **1982**, *21*, 1389. (b) Dewan, J. C. *Acta Crystallogr., Sect. C* **1988**, *C44*, 2199.
(18) (a) Drew, M. G. B.; Dunlop, J. H.; Gillard, R. D.; Rogers, D *J. Chem. Soc., Chem. Commun.* **1966**, 42. (b) Herak, R.; Prelesnik, B.; Krstanovic, I. *Acta Crystallogr., Sect. B* **1978**, *34*, 91.
(19) Soling, H. *Acta Chem. Scand.* **1978**, *A32*, 361.
(20) Bryan, R. F.; Greene, P. T.; Stokely, P. F.; Wilson, E. W., Jr. *Inorg. Chem.* **1971**, *10*, 1468.
(21) Mazzanti, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 356. Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 4158. Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1793. Rosset, J.-M.; Floriani, C.; Mazzanti, M.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1989**, *29*, 3991.

Table III. Fractional Atomic Coordinates (×10⁴) for Complex **1**[a]

	molecule A			molecule B		
atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
V1	151.9(11)	0	-989.9(10)	-2873.15(11)	-1415.6(7)	3585.6(10)
O1	682(5)	-357(3)	722(4)	-3086(5)	-1101(3)	1892(4)
O2	1050(5)	898(3)	-557(5)	-3582(5)	-2352(3)	3250(5)
O3	-773(4)	111(2)	-2772(4)	-2575(4)	-1431(3)	5363(4)
O4	403(5)	-1109(3)	2110(4)	-2827(5)	-308(3)	610(4)
O5	2914(7)	1507(3)	-110(7)	-2992(7)	-3461(3)	3455(7)
O6	-2629(5)	421(3)	-4280(5)	-3426(5)	-1259(3)	6876(4)
N1	-728(5)	-1044(3)	-1229(5)	-1987(6)	-394(3)	3883(5)
N2	2118(6)	-242(3)	-1112(5)	-1065(6)	-1956(3)	3569(5)
N3	-1716(6)	453(3)	-970(5)	-4751(6)	-974(3)	3563(5)
C1	-111(8)	-1565(4)	-1838(7)	-478(8)	-328(5)	4442(7)
C2	-409(9)	-2259(4)	-1378(8)	-145(10)	379(5)	4129(8)
C3	-221(11)	-2108(4)	-22(9)	-1070(9)	467(4)	2801(8)
C4	-707(7)	-1352(4)	-46(7)	-2327(7)	11(4)	2700(7)
C5	188(7)	-913(4)	1029(6)	-2774(7)	-487(4)	1636(7)
C6	2228(8)	-212(4)	-2385(8)	15(8)	-2147(5)	4743(7)
C7	3734(8)	-43(5)	-2146(10)	496(12)	-2831(5)	4566(13)
C8	4164(8)	383(6)	-1051(10)	-347(10)	-3134(5)	3453(9)
C9	3077(7)	302(4)	-397(8)	-1527(8)	-2645(4)	2957(7)
C10	2336(8)	951(5)	-346(7)	-2774(9)	-2870(4)	3258(7)
C11	-1643(9)	1193(4)	-460(8)	-6033(8)	-1337(5)	2754(7)
C12	-2991(12)	1544(8)	-1165(13)	-6462(9)	-1785(6)	3636(10)
C12′	-2314(22)	1636(11)	-1420(18)			
C13	-3353(9)	1206(4)	-2426(8)	-6099(9)	-1353(6)	4806(8)
C14	-2692(6)	484(4)	-2252(6)	-4834(7)	-958(4)	4826(6)
C15	-2008(6)	342(3)	-3174(6)	-3526(7)	-1238(4)	5783(6)
S1	4315(3)	-2241(2)	-417(3)	3956(3)	792(2)	3703(3)
S1′	3969(28)	-2114(16)	-1613(27)	4043(31)	1200(17)	2990(30)
O7	3264(7)	-1683(4)	-672(8)	4646(6)	490(3)	2865(5)
C21	5672(9)	-1932(6)	-841(9)	2323(9)	1104(6)	2671(10)
C22	3741(12)	-2906(6)	-1556(12)	4675(12)	1632(6)	4200(10)

[a] The site occupation factors for the disordered atoms are 0.6 and 0.4 for C12 and C12′ and 0.9 and 0.1 for S1 and S1′, respectively.

Table IV. Fractional Atomic Coordinates (×10⁴) for Complex **2**[a]

	molecule A			molecule B		
atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
V1	152.4(7)	0(–)	-988.4(6)	-2871.9(7)	1416.4(5)	3581.9(6)
O1	676(3)	357(2)	726(3)	-3086(4)	1098(2)	1893(3)
O2	1054(4)	-891(2)	-554(4)	-3588(4)	2352(2)	3254(4)
O3	-762(3)	-114(2)	-2767(3)	-2568(3)	1428(2)	5364(3)
O4	400(4)	1111(2)	2111(3)	-2816(4)	309(2)	604(3)
O5	2913(5)	-1519(3)	-110(5)	-2993(6)	3464(3)	3471(6)
O6	-2620(4)	-424(2)	-4284(3)	-3421(4)	1252(2)	6865(3)
N1	-719(3)	1045(2)	-1230(3)	-1973(4)	392(2)	3888(3)
N2	2109(4)	249(2)	-1131(4)	-1068(4)	1959(2)	3570(4)
N3	-1720(4)	-462(2)	-953(3)	-4764(4)	971(2)	3549(3)
C1	-96(5)	1573(3)	-1839(5)	-462(6)	339(3)	4445(5)
C2	-407(6)	2265(3)	-1383(6)	-144(7)	-380(4)	4115(6)
C3	-231(8)	2111(3)	-50(7)	-1056(6)	-465(3)	2804(6)
C4	-696(4)	1356(3)	-32(4)	-2313(5)	-19(3)	2720(4)
C5	196(4)	919(3)	1030(4)	-2764(4)	489(3)	1634(4)
C6	2252(5)	213(3)	-2359(6)	5(6)	2139(4)	4748(5)
C7	3742(6)	70(4)	-2150(8)	473(10)	2836(5)	4594(10)
C8	4156(5)	-380(5)	-1053(8)	-342(8)	3138(4)	3442(7)
C9	3071(5)	-296(3)	-396(5)	-1534(6)	2648(3)	2965(5)
C10	2343(5)	-956(3)	-352(5)	-2795(6)	2867(3)	3262(6)
C11	-1653(6)	-1177(3)	-444(6)	-6028(5)	1339(4)	2766(5)
C12	-2938(9)	-1529(5)	-1139(9)	-6425(6)	1797(4)	3626(7)
C12′	-2303(13)	-1659(6)	-1503(10)			
C13	-3342(6)	-1210(3)	-2412(5)	-6102(6)	1349(5)	4787(6)
C14	-2700(4)	-485(2)	-2260(4)	-4820(5)	954(3)	4842(4)
C15	-1988(4)	-336(2)	-3178(4)	-3528(5)	1233(3)	5767(4)
S1	4326(2)	2242(1)	-412(2)	3962(2)	-795(1)	3700(2)
S1′	3966(18)	2060(10)	-1528(17)	4056(19)	-1209(10)	2996(18)
O7	3280(5)	1680(3)	-659(7)	4664(5)	-500(3)	2862(4)
C21	5680(6)	1936(4)	-845(7)	2341(7)	-1090(5)	2688(8)
C22	3784(9)	2922(5)	-1539(9)	4684(10)	-1634(6)	4194(8)

[a] The site occupation factors for the disordered atoms are 0.6 and 0.4 for C12 and C12′, and 0.9 and 0.1 for S1 and S1′ respectively.

While there is no evidence for intramolecular hydrogen bonding, all the three N–H groups for each independent molecule are engaged in the formation of intermolecular N–H···O hydrogen bonds. Two of these involve the carbonylic oxygen atoms of adjacent molecules and link the molecules in finite chains running parallel to the [001] axis (Figure 4). The chains are delimited by N–H···O hydrogen bonds involving the oxygen atoms of the DMSO molecules (Table VII) and are seperated by van der Waals

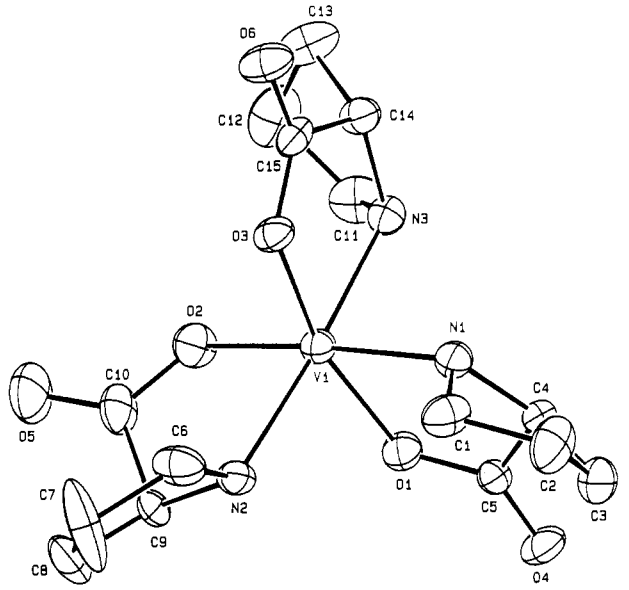


Figure 1. ORTEP drawing of complex **1**, molecule B (30% probability ellipsoids).

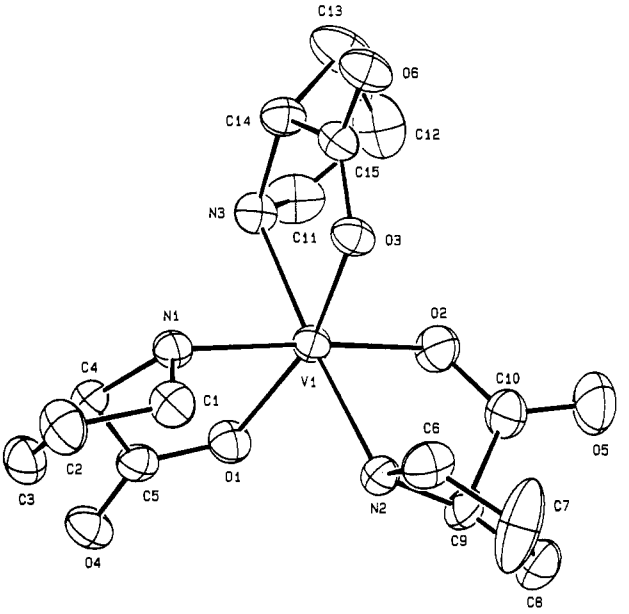


Figure 2. ORTEP drawing of complex **2**, molecule B (30% probability ellipsoids).

interactions. A chain arrangement was also seen in the structure of tris(L-alaninato)cobalt(III) monohydrate.[18b] The solvent of crystallization serves to break down the three dimensional network into linear structures.

Complex **2** is isostructural with complex **1**. The two independent vanadium atoms occupy the same position in the crystal lattice, but owing to the different chirality of the amino acid, the two different A and B molecules in complex **2** are the enantiomers of the corresponding ones in complex **1**. They assume therefore a *mer* Λ configuration as can be seen from Figure 3 where the configurations of the two complexes are compared. In Figure 6 we show the four isomers of **2**. If molecules **1** and **2** are compared, the A and B pairs are seen to be almost identical. However differences exist between molecules A and B of the same complex, as emphasized from the data in Tables IV and V. The shortest intraligand contact concerns the C11 and O2 atoms. This contact is significantly shorter in the A than in the B molecules: C11A···O2A, 2.913(12) Å [complex **1**] and 2.934(8) Å [complex **2**]; C11B···O2B, 3.116(10) Å [complex **1**] and 3.109(7)Å [complex **2**]. These differences are probably related to the

Table V. Selected Bond Distances (Å) and Angles (deg) for Complexes **1** and **2**

	complex 1		complex 2	
	molecule A	molecule B	molecule A	molecule B
V1–O1	1.974(5)	1.971(5)	1.980(4)	1.971(4)
V1–O2	1.942(6)	1.928(6)	1.933(4)	1.929(4)
V1–O3	1.960(4)	1.954(5)	1.958(3)	1.962(4)
V1–N1	2.178(6)	2.141(6)	2.177(4)	2.152(4)
V1–N2	2.159(7)	2.162(7)	2.164(5)	2.162(4)
V1–N3	2.146(7)	2.131(7)	2.166(4)	2.148(4)
O1–C5	1.281(10)	1.278(10)	1.283(7)	1.275(7)
O2–C10	1.291(10)	1.301(10)	1.300(7)	1.287(7)
O3–C15	1.298(7)	1.294(10)	1.286(5)	1.294(7)
O4–C5	1.240(8)	1.207(10)	1.242(6)	1.214(6)
O5–C10	1.209(11)	1.189(10)	1.218(8)	1.199(8)
O6–C15	1.227(8)	1.221(9)	1.233(5)	1.227(6)
N1–C1	1.481(11)	1.501(10)	1.496(7)	1.503(7)
N1–C4	1.470(10)	1.497(10)	1.490(6)	1.491(6)
N2–C6	1.500(12)	1.488(9)	1.467(9)	1.485(6)
N2–C9	1.489(9)	1.496(9)	1.501(6)	1.494(7)
N3–C11	1.523(10)	1.523(9)	1.480(7)	1.507(6)
N3–C14	1.487(8)	1.477(10)	1.512(5)	1.504(6)
N2–V1–N3	168.2(2)	174.7(2)	168.3(1)	174.5(2)
N1–V1–N3	91.3(2)	89.4(3)	91.8(1)	89.6(2)
N1–V1–N2	99.7(2)	95.9(3)	99.0(1)	95.8(2)
O3–V1–N3	80.1(2)	81.3(2)	80.8(1)	81.6(1)
O3–V1–N2	96.3(2)	99.3(2)	95.5(2)	99.2(2)
O3–V1–N1	85.7(2)	86.3(2)	85.9(1)	85.9(1)
O2–V1–N3	90.4(2)	94.2(3)	90.3(2)	93.8(2)
O2–V1–N2	79.3(3)	80.5(2)	79.5(2)	80.7(2)
O2–V1–N1	172.7(2)	175.7(3)	172.5(2)	176.1(2)
O2–V1–O3	101.6(2)	96.4(2)	101.5(2)	96.4(2)
O1–V1–N3	95.0(1)	93.6(2)	94.4(1)	93.2(2)
O1–V1–N2	91.6(2)	87.3(2)	92.3(1)	87.6(2)
O1–V1–N1	77.1(2)	77.3(2)	77.1(1)	77.3(1)
O1–V1–O3	162.0(2)	162.9(3)	162.2(1)	162.5(2)
O1–V1–O2	95.7(2)	100.2(2)	95.5(2)	100.6(2)
V1–O1–C5	123.5(4)	123.5(4)	123.6(3)	123.9(3)
V1–O2–C10	120.3(6)	120.0(6)	121.4(3)	120.0(4)
V1–O3–C15	119.9(4)	120.3(4)	120.3(3)	119.4(3)
V1–N1–C4	112.0(4)	111.5(4)	111.8(3)	111.8(3)
V1–N1–C1	116.3(5)	119.0(5)	116.7(3)	118.3(3)
C1–N1–C4	106.7(5)	104.2(6)	106.5(4)	104.6(4)
V1–N2–C9	107.4(5)	106.0(5)	106.4(3)	105.9(3)
V1–N2–C6	115.8(5)	121.0(5)	117.6(3)	120.5(3)
C6–N2–C9	104.7(6)	103.8(6)	104.1(4)	104.5(4)
V1–N3–C14	109.7(4)	110.4(4)	108.4(3)	109.2(3)
V1–N3–C11	116.6(5)	116.8(5)	117.4(3)	116.8(3)
C11–N3–C14	105.8(6)	106.3(6)	107.0(4)	106.5(4)

disorder in the pyrrolidinic ring N3,C11,C12,C13,C14 of the A molecules of both compounds. The C12A atoms are statistically distributed over two positions corresponding to different ring conformations. Between molecules A and B, there are also differences in the dihedral angles of the chelation rings (Table V).

Optical rotations were measured for all of the complexes, and values for $[\alpha]_D^{20}$ are given in Table I. The angles of rotation are very high when compared with the values for the uncomplexed α-amino acids ($[\alpha]_D^{20}$: L-pro, −85.0°; D-pro, +81.5°; L-Phe, −35.1°; D-Phe, +35.0°; L-Trp, +31.5°; L-Val, +28.8°). Interestingly, the direction of rotation observed for the L-prolinato complex **1** is opposite to that seen for the complexes of L-Phe, L-Trp, and L-Val. This suggests that these latter complexes assume another of the four isomeric forms shown in Figure 5. Although in the cases of **1** and **2** only one of four possible diastereoisomers was crystallized, we believe that in the reaction solution more than one isomer may be present. This is evidenced by the fact that the optical rotation measured for the reaction solution giving **1** ($[\alpha]_D^{20}$ = +228°) is significantly less than that for pure **1**. The complexes have magnetic moments that are close to the value expected for V(III) (2.83 μ_B). Their infrared spectra are characterized by a strong ν(C–O) band between 1636 and 1651 cm^{-1}.

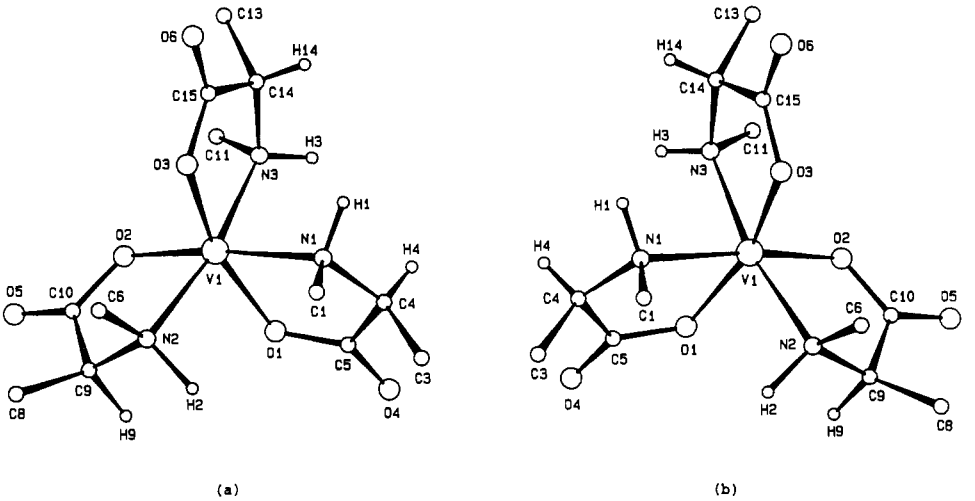


Figure 3. Simplified picture of the enantiomeric complexes **1** and **2** (a) showing the *mer* Δ diasteriomeric form of tris(L-prolinato)vanadium (complex **1**) and (b) the *mer* Λ diasteriomeric form of tris(D-prolinato)vanadium (complex **2**).

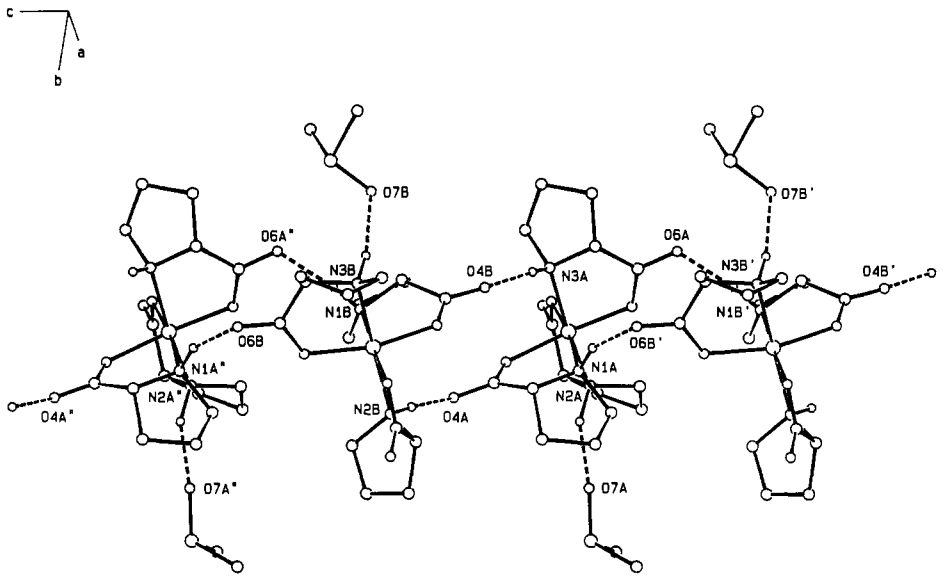


Figure 4. Projection of the network of hydrogen bonds.

We are currently investigating the reactivity of these compounds.

Experimental Section

General Procedure. All operations were carried out under an atmosphere of purified nitrogen using modified Schlenk techniques or in a Braun drybox. Solvents were dried and distilled before use by standard methods. The compound $[V(Mes)_3(THF)]$ was prepared as reported.[22] α-Amino acids (Fluka) were dried by stirring in refluxing anhydrous THF for several hours, after which traces of water were distilled off with the THF. The $[\alpha]_D^{20}$ measurements were made with a Perkin-Elmer 241 polarimeter. Magnetic measurements were carried out at room temperature using a Sherwood Scientific MSB Gouy balance. Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer.

Synthesis of [V(L-Pro)$_3$]·DMSO, 1·DMSO. To a THF (150 mL) solution of $[V(Mes)_3(THF)]$ (3.431 g, 7.15 mmol) was added L-proline (2.901 g, 25.23 mmol). After 24 h, the blue solution became clear and a brown precipitate had formed. After evaporation of the solvent, the residue was extracted with DMSO (30 mL), which was then filtered to remove traces of unreacted L-proline. The rose-colored solution was layered with Et_2O (50 mL) and THF (10 mL) resulting in the precipitation after 24 h of rose-colored V(L-Pro)$_3$·DMSO (1.953 g, 58%). Recrystallization from DMSO/Et_2O gave crystals suitable for X-ray analysis. Anal. Calcd for $C_{17}H_{30}N_3O_7SV$: C, 43.31; H, 6.41; N, 8.91. Found: C, 43.51; H, 6.71; N, 8.66. IR (Nujol): ν(CO) 1636 cm^{-1}. μ_{eff}: 2.58 μ_B. $[\alpha]_D^{20}$: 312°.

Synthesis of [V(D-Pro)$_3$]·DMSO, 2·DMSO. To a THF (75 mL) solution of $[V(Mes)_3(THF)]$ (1.35 g, 2.81 mmol) was added D-proline (1.00 g, 8.70 mmol). A brown precipitate formed after 24 h. The solvent was evaporated and the brown residue extracted into DMSO (20 mL). After filtration to remove traces of unreacted D-proline, the rose-colored solution was layered with Et_2O (30 mL) and THF (10 mL), resulting in the precipitation of rose-colored V(D-Pro)$_3$·DMSO (0.717 g, 55%). Recrystallization from DMSO/Et_2O gave X-ray quality crystals. Anal. Calcd for $C_{17}H_{30}N_3O_7SV$: C, 43.31; H, 6.41; N, 8.91. Found: C, 43.06; H, 6.73; N, 8.72. IR (Nujol): ν(CO) 1634 cm^{-1}. μ_{eff}: 2.62 μ_B. $[\alpha]_D^{20}$: −318°.

Synthesis of [V(L-Phe)$_3$]·THF, 3·THF. To a THF (200 mL) solution of $[V(Mes)_3(THF)]$ (5.212 g, 10.86 mmol) was added L-phenylalanine (5.396 g, 32.70 mmol). After 72 h, a pale brown solution was obtained which, after filtration to remove traces of unreacted L-Phe, was concentrated to 100 mL and layered with Et_2O (100 mL), resulting in the precipitation of $[V(L\text{-}Phe)_3(THF)]$ as a pale pink solid (4.369 g, 65%). The product was recrystallized from THF/Et_2O. Anal. Calcd for $C_{31}H_{38}N_3O_7V$: C, 60.48; H, 6.22; N, 6.83. Found: C, 60.94; H, 5.96; N, 6.42. IR(Nujol): ν(CO) 1651 cm^{-1}. μ_{eff}: 2.61 μ_B. $[\alpha]_D^{20}$: −276°.

Synthesis of [V(D-Phe)$_3$]·THF, 4·THF. To a THF (150 mL) solution of $[V(Mes)_3(THF)]$ (3.002 g, 6.25 mmol) was added D-phenylalanine (3.140 g, 19.03 mmol). After 72 h, a pale brown solution was obtained which, after filtration to remove traces of unreacted D-Phe, was concentrated to 100 mL and layered with Et_2O (100 mL), resulting in

(22) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1984**, 886.

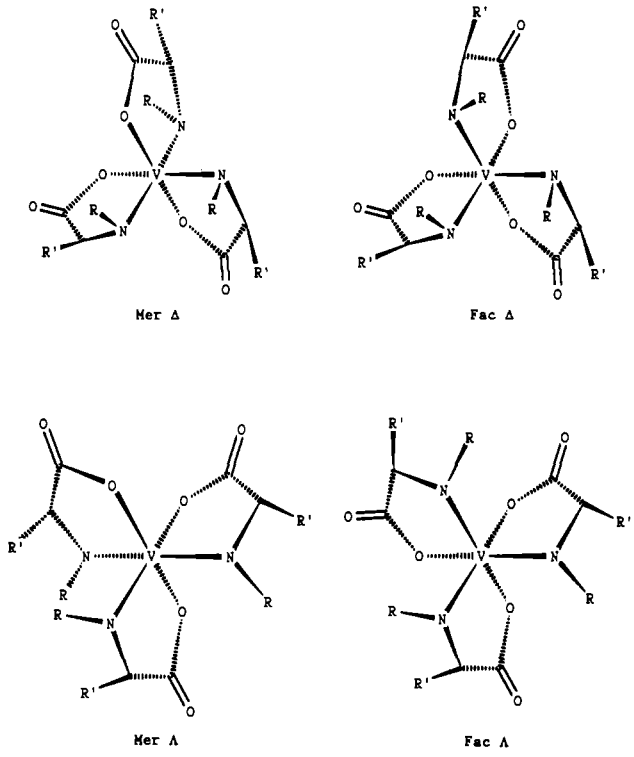


Figure 5. The four possible isomeric forms of tris(L-prolinato) vanadium(III).

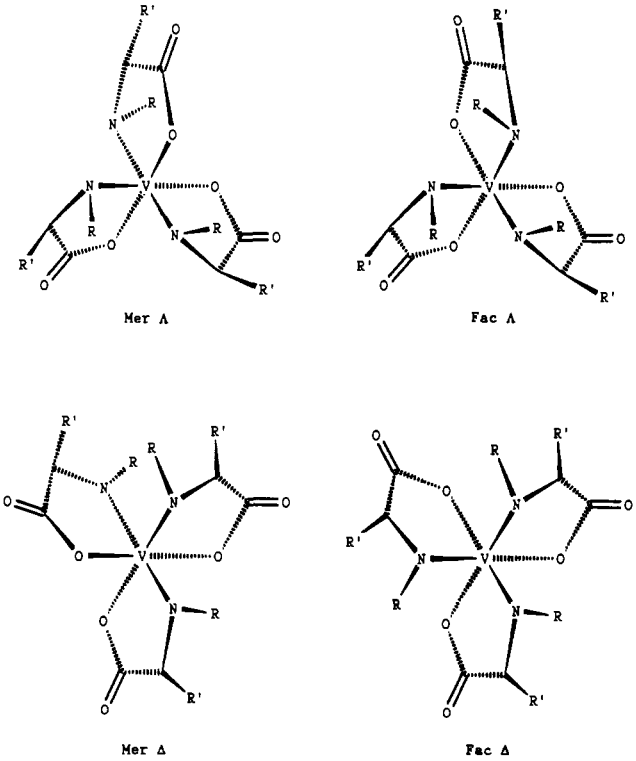


Figure 6. The four possible isomeric forms of tris(D-prolinato) vanadium(III).

the precipitation of [V(D-Phe)$_3$(THF)] as a rose-colored solid (2.519 g, 66%). The product was recrystallized from THF/Et_2O. Anal. Calcd for $C_{31}H_{38}N_3O_7V$: C, 60.48; H, 6.22; N, 6.83. Found: C, 59.81; H, 5.90; N, 7.65. IR(Nujol): ν(CO) 1651 cm^{-1}. μ_{eff}: 2.67 μ_B. $[\alpha]_D^{20}$: 272°.

Synthesis of [V(DL-Phe)$_3$]·THF, 5·THF. To a THF (100 mL) solution of [V(Mes)$_3$(THF)] (1.637 g, 3.41 mmol) was added DL-phenylalanine (1.687 g, 10.22 mmol). After 96 h, a red-brown solution was obtained, which after filtration to remove traces of unreacted DL-Phe was concentrated to 50 mL and layered with Et_2O (75 mL) resulting in the precipitation of [V(DL-Phe)$_3$(THF)] as a dark brown solid (1.048 g, 50%). The product was subsequently insoluble in THF. Anal. Calcd for $C_{31}H_{38}N_3O_7V$: C, 60.48; H, 6.22; N, 6.83. Found: C, 58.88; H, 6.00; N, 6.00. IR(Nujol): ν(CO) 1581 cm^{-1}. μ_{eff}: 3.09 μ_B. $[\alpha]_D^{20}$: 0°.

Synthesis of [V(L-Trp)$_3$]·THF, 6·THF. To a THF (100 mL) solution of [V(Mes)$_3$(THF)] (1.816 g, 3.78 mmol) was added L-tryptophan (2.32 g, 11.37 mmol). After 24 h, a red precipitate was obtained which was collected by filtration. The solid was then placed on an extracting filter and extracted with refluxing THF (50 mL) over 7 days, giving [V(L-Trp)$_3$(THF)] as a pale pink solid (1.703 g, 61%). Anal. Calcd for $C_{37}H_{41}N_6O_7V$: C, 60.65; H, 5.64; N, 11.47. Found: C, 60.53; H, 5.70; N, 11.57. IR(Nujol): ν(CO) 1645 cm^{-1}. μ_{eff}: 2.55 μ_B. $[\alpha]_D^{20}$: −148°.

Synthesis of [V(L-Val)$_3$]·2DMSO, 7·(DMSO)$_2$. To a THF (100 mL) solution of [V(Mes)$_3$(THF)] (1.997 g, 4.16 mmol) were added L-valine (1.503 g, 12.85 mmol) and a pinch of LiCl. After 48 h, a brown precipitate had formed. After evaporation of the solvent, the residue was extracted with DMSO (20 mL) which was then filtered to remove traces of unreacted L-valine. The brown solution was layered with Et_2O (50 mL) and THF (10 mL) resulting in the precipitation after 24 h of rose-colored V(L-Val)$_3$·2DMSO (0.572 g, 25%). Anal. Calcd for $C_{19}H_{42}N_3O_8S_2V$: C, 41.07; H, 7.62; N, 7.56. Found: C, 41.31; H, 7.86; N, 7.74. IR (Nujol): ν(CO) 1643 cm^{-1}. μ_{eff}: 2.73 μ_B. $[\alpha]_D^{20}$: −158°.

Crystal Structure Determinations of Complexes 1·DMSO and 2·DMSO. Crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Crystal data and details associated with the structure refinement are given in Table II. The reduced cells were obtained using TRACER.[23] The data was collected at room temperature on a single-crystal four circle diffractometer. For intensities and background, individual reflection profiles were analyzed.[24] The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[25] and the absolute scale was established by the Wilson method.[26] Intensity data were corrected for absorption using a semi-empirical method[27] based on a ψ scan for complex **1** and ABSORB[28] for complex **2**. The function minimized during the full matrix least-squares refinement was $\sum w|\Delta F|^2$.

Table VI. Comparison of Conformational Parameters for Complexes **1** and **2**

	1		2	
	mol A	mol B	mol A	mol B
	Plane 1: N1,C4,C5,O1			
dist of N1,C4,C5,O1,V from the NC_2O plane, Å	−0.006(6)	−0.032(7)	−0.007(4)	−0.035(4)
	0.018(8)	0.078(8)	0.023(5)	0.098(6)
	−0.020(8)	−0.089(8)	−0.026(5)	−0.078(5)
	0.007(6)	−0.029(6)	0.009(4)	0.043(4)
	0.329(3)	0.276(3)	0.318(1)	0.268(1)
	Plane 2: N2,C9,C10,O2			
dist of N2,C9,C10,O2,V from the NC_2O plane, Å	0.025(6)	−0.056(6)	0.036(4)	−0.053(4)
	−0.109(9)	0.202(8)	−0.110(6)	0.162(6)
	0.107(8)	−0.227(8)	0.122(6)	−0.257(6)
	−0.030(6)	0.069(6)	−0.044(4)	0.067(4)
	−0.430(2)	0.230(2)	−0.411(6)	0.280(1)
	Plane 3: N3,C14,C15,O3			
dist of N3,C14,C15,O3,V from the NC_2O plane, Å	0.021(6)	0.001(6)	0.024(4)	0.002(4)
	−0.066(8)	−0.004(8)	−0.045(4)	−0.007(6)
	0.045(6)	0.004(8)	0.051(4)	0.008(6)
	−0.012(4)	−0.001(6)	−0.028(4)	−0.002(4)
	−0.160(1)	0.092(2)	−0.219(1)	0.090(1)
angle between planes 1 and 2, deg	89.5(4)	85.5(3)	90.0(2)	84.1(1)
angle between planes 1 and 3, deg	77.3(3)	83.6(4)	76.4(2)	83.9(2)
angle between planes 2 and 3, deg	63.5(3)	81.9(4)	62.7(2)	80.4(3)

(23) Lawton, S. L.; Jacobson, R. A. "TRACER", a cell reduction program. Ames Laboratory, Iowa State University of Science and Technology, 1965.
(24) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1974**, *A30*, 580.
(25) Data reduction, structure solution, and refinement were carried out on an IBM AT personal computer equipped with an Inmos T800 Transputer using: G. Sheldrick, SHELX-76. System of Crystallographic Computer Programs. University of Cambridge; Cambridge, England, 1976.
(26) Wilson, A. J. C. *Nature (London)*, **1942**, *150*, 151.
(27) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1968**, *A24*, 351.
(28) Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

Table VII. Intermolecular Hydrogen Bonds for Complexes **1** and **2**[a]

	complex 1	complex 2		complex 1	complex 2
N1A···O6B′	2.968(7) Å	2.977(4)	N1A–H1A···O6B	155.6	156.0
N2A···O7A	2.981(10)	2.976(7)	N2A–H2A···O7A	144.0	152.0
N3A···O4B	2.851(9)	2.836(6)	N3A–H3A···O4B	168.1	168.9
N1B···O6A″	2.870(9)	2.870(6)	N1B–H1B···O6A	159.9	164.1(3)
N2B···O4A	3.077(9)	3.083(6)	N2B–H2B···O4A	173.6	176.9
N3B···O7B	2.923(8)	2.930(7)	N3B–H3B···O7B	159.5	162.1

[a] Symmetry key: single prime, $x, y, z - 1$; double prime, $x, y, z + 1$.

Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|F_o)^2]$. Scattering factors for neutral atoms were taken from ref 29a for non-hydrogen atoms and from ref 30 for hydrogen. Anomalous scattering corrections were included in all structure factor calculations.[29b] Among the low-angle reflections, no correction for secondary extinction was deemed necessary.

Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from three dimensional Patterson maps. Refinement was first done isotropically, then anisotropically for all non-hydrogen atoms except for the disordered groups (*vide infra*). The C12 methylene carbon atom (molecule A) of complexes **1** and **2** was found to be affected by a conformational disorder and statistically distributed over two positions isotropically refined with sight occupation factors of 0.6 and 0.4 for C12 and C12′, respectively. During the refinement, a constraint (C–C = 1.54(1) Å) was applied to the C11–C12′ distance of both complexes.

At the end of the refinement, residue peaks of ~1.2 e Å^{-3} were found in the regions of the DMSO molecules for both complexes. They were interpreted as "partial" sulfur atoms corresponding to the enantiomeric forms of DMSO. The best fit was found by considering the sulfur atoms (for each DMSO in both complexes) to be statistically distributed over two positions with site occupation factors of 0.9 and 0.1 for the unprimed and primed positions respectively. The primed positions were isotropically refined. All the hydrogen atoms, except those associated with the disordered C12 atoms and the DMSO molecules, which were ignored, were located from a ΔF map and introduced as fixed contributors prior to the last stage of refinement (U_{iso} = 0.10 Å^2). At first, the absolute configuation was chosen by comparison with that of the L-prolinato ligand. It was then unambiguously established for both complexes by inverting all the coordinates ($x,y,z \rightarrow -x,-y,-z$) and refining to convergence once again. The resulting R values (R = 0.048, R_G = 0.065 for complex **1**; R = 0.050, R_G = 0.084 for complex **2**) confirmed the original choice to be the correct one.

Final atomic coordinates are listed in Tables III and IV for non-hydrogen atoms; selected bond distances and angles are quoted in Table V.[31]

Acknowledgment. We would like to thank the Fonds National Suisse de la Recherche Scientifique (Grant. No. 20-33420-92) and the Fondation Herbette (University of Lausanne) for financial support.

Supplementary Material Available: Listings of experimental details associated with data collection (Table SI), unrefined hydrogen coordinates (Tables SII and SIII), thermal parameters (Tables SIV and SV), and bond distances and angles (Tables SVI and SVII) (12 pages). Ordering information is given on any current masthead page.

(29) *International Tables for X-ray Crystallography*; Kynoch Press; Birmingham, England, 1974; Vol. IV: (a) p 9 (b) p 149.
(30) Stewart, R. F.; Davidson, F. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(31) See the paragraph at the end of the paper regarding supplementary material.