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Atropisomerism in Metal Chelates. Crystal Structure of $[(+)_{589}$-3-(1-Naphthyl)pentane-2,4-dionato][tris(2-aminoethyl)amine]cobalt(III) Bis(tetrafluoroborate) Dihydrate[1]

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The crystal structure and the absolute configuration of $[(+)_{589}$-3-(1-naphthyl)pentane-2,4-dionato][tris(2-aminoethyl)amine]cobalt(III) bis(tetrafluoroborate) dihydrate were determined by X-ray diffraction. The complex crystallizes in orthorhombic space group $P2_12_12_1$ with $a = 10.286$ (1), $b = 33.077$ (4), and $c = 8.495$ (2) Å and $Z = 4$. The structure was solved by the Patterson-Fourier method and refined to a final R_1 value of 0.060 for the 2760 observed reflections with $|F_o| > 3\sigma(|F_o|)$. The naphthalene ring is almost perpendicular to the coordination plane of acac ring, and the latter adopts planar conformation. One of the three five-membered chelate rings formed by the tren chain exhibits a conformational disorder, where planar conformation is predominant. The other two chelate rings take envelope conformation. The absolute configuration of the present complex can be designated as *R*.

Introduction

The optical activity of the atropisomers arises from the restricted rotation of the aromatic ring. Crystal structure and absolute configuration of the two members of this series were determined recently (complex II[3] and III[4] in Figure 1). In the two complexes, the acac ring adopts the boat conformation as shown in Figure 2. Interactions between amino and *o*-nitro groups seem to deform the ring. Absolute configurations of the levorotatory isomers of the complex II and III are designated as *R*.[5]

Advantages over the two complexes II and III are expected for the present complex in the study of the stereochemistry as well as electronic states of these complexes. The first advantage is that the absence of polar substituents on the aromatic ring excludes the possibility of nonbonding interactions mentioned above. The second is that the electronic states of naphthalene ring which cause the asymmetry of the present complex have been established completely. Accordingly the crystal structure and absolute configuration were determined by X-ray diffraction.

Experimental Section

The title compound was obtained by addition of excess sodium tetrafluoroborate to the aqueous solution of complex I ion.[6] The crystal were reddish brown plates. Crystal data and data collection details are summarized in Table I. The structure was solved by the heavy-atom method. All the nonhydrogen atoms were refined by a block-diagonal least squares with anisotropic thermal parameters. Hydrogen atoms were located from the difference Fourier maps, except eight hydrogen atoms of the A ring (see Figure 1) and the water molecules, and were included in the refinement with isotropic thermal parameters. At a late stage of the refinement, a carbon atom of the tren chain and three fluorine atoms of one tetrafluoroborate ion were found to have disordered dispositions. Separation of the carbon and three fluorine atoms atoms reduced the values of R_2 by 0.001 and 0.007, respectively, where $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = [\sigma^2(|F_o|) + (0.020|F_o|)^2]^{-1}$. Thus the regular structure can be rejected at the 0.005 significance level by the Hamilton's *R* test.[7] The disordered model was refined by the full-matrix least squares to final R_1 of 0.060 and R_2 of 0.068.[8,9]

Table I

Crystallographic Summary

$C_{21}H_{35}B_2CoF_8N_4O_4$	mol wt 640.07
orthorhombic	$P2_12_12_1$
$a = 10.286$ (1), $b = 33.077$ (2), $c =$ 8.495 (2) Å[a]	$V = 2890.4$ (7) Å^3
$d_{\text{calcd}} = 1.43$, $d_{\text{measd}} = 1.47$ g/cm^3	$Z = 4$
$\mu = 7.0\%$ cm^{-1}	

Data Collection (at 25 °C)

cryst dimens	0.25 × 0.33 × 0.48 mm
diffractometer	Rigaku AFC-3 automated four-circle diffractometer
radiation	Mo Kα (monochromated with graphite), λ = 0.710 69 Å
data collection range	$3 < 2\theta < 55°$
scan mode	ω-2θ scan(2°/min in ω)
total data collected	3277 (+*h*,+*k*,+*l*)
data with $|F_o| > 3\sigma(|F_o|)$	

[a] The latice constants were obtained by a least-squares calculation based on 40 reflections with $16.1 < \theta < 19.4°$.

The final positional parameter shift of *z* component of *F*(3) was 1.5σ. Those of the other nonhydrogen atoms were less than 0.8σ. The final difference Fourier maps showed no peaks greater than 0.5 e/Å^3. There remained several peaks (0.3–0.5 e/Å^3) around the B(1) atom. The positional and thermal parameters along with their standard deviations are listed in Table II and Table III,[8] respectively.

The absolute configuration was determined by anomalous scattering technique. Some Bijvoet pairs were examined on equiinclination Weissenberg photographs taken with Cu Kα radiation. The observed and calculated differences are compared in Table IV,[8] for which $|F_c(hkl)|$ and $|F_c(h\bar{k}l)]$ differed by more than 35%. The concordance in the table indicated that the absolute configuration of $(+)_{589}$ isomer is R^5. So that this could be confirmed, result residuals of the *R* configuration were compared with that of the *S* configuration at a stage that all the nonhydrogen atoms were located. They were $R_1 = 0.074$ and $R_2 = 0.082$, while those of the *S* configuration were $R_1 = 0.077$ and $R_2 = 0.085$. Application of the *R* factor ratio test shows that the *S* configuration can be rejected at the 0.005 significance level in favor of *R* configuration.[7]

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(1) The following abbreviations were used: tren, tris(2-aminoethyl)amine; acacH, acetylacetone.
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(3) Nakano, Y.; Sato, S., submitted for publication in *Bull. Chem. Soc. Jpn.*
(4) Nakano, Y.; Sato, S. *Inorg. Chem.* **1980**, *19*, 3391.
(5) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.
(6) Kondo, H.; Nakano, Y., unpublished data.
(7) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.
(8) Supplementary material.
(9) The atomic scattering factors and anomalous scattering corrections were taken from "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4. The calculations were performed on a FACOM 230-48 computer at this institute with a local version of UNICS ("Universal Crystallographic Computation Program System"; Sakurai, T., Ed.; The Crystallographic Society of Japan: Tokyo, Japan, 1967).

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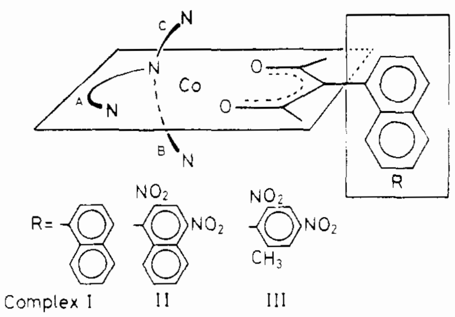

Figure 1.

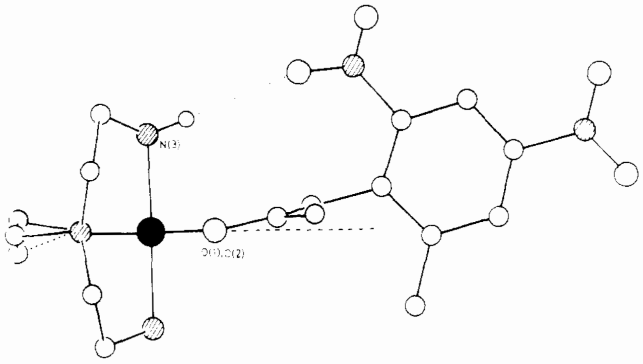

Figure 2. Projection of complex III along the line of O(1)–O(2).

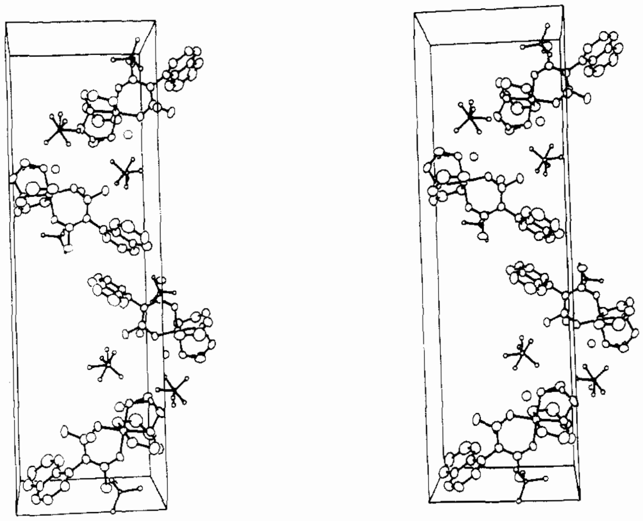

Figure 3. Stereoview of the unit cell along the *c* axis.

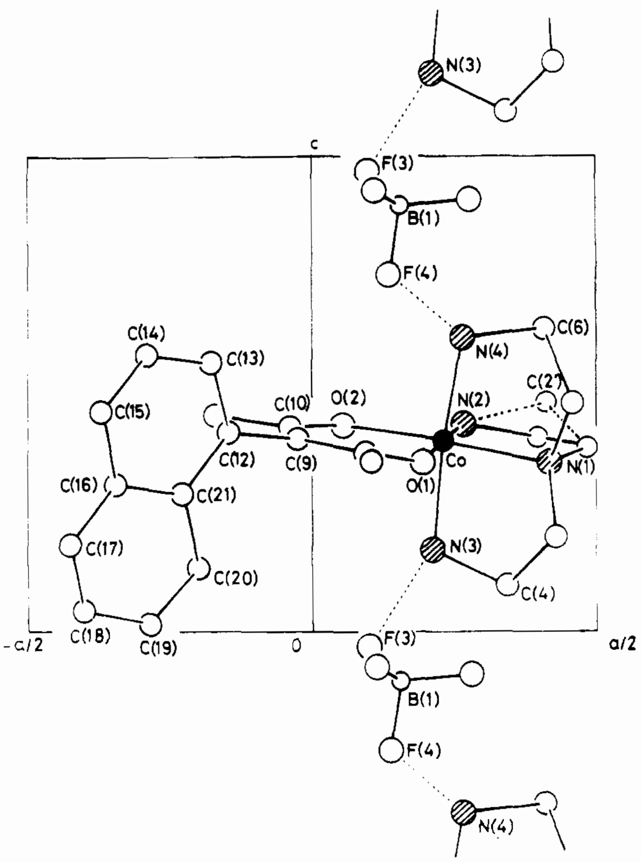

Figure 4. Projection of the crystal structure along the *b* axis.

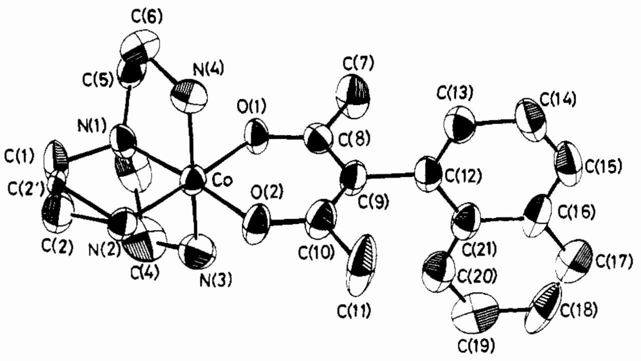

Figure 5. Perspective drawing of complex I and the numbering scheme for the atoms.

Description of the Structure and Discussion

Figure 3 shows a stereoview of the unit cell along the *c* axis showing an arrangement of the four complex cations, the eight tetrafluoroborate ions, and eight water molecules of crystallization in the unit cell. Figure 4 gives a projection of the crystal structure along the *b* axis. The complex cations are linked in chain along the *c* axis through the hydrogen bonds between the tetrafluoroborate ions and the amino groups (as shown in Figure 4). Since the thermal parameters of the atoms of the tetrafluoroborate ion are considerably large, the hydrogen bonds (N–H···F) may be weak. The other tetrafluoroborate ion is bound to the amino group through a hydrogen bond, although the key hydrogen atom could not be found because of disordered structure of the A ring (see Figure 1). The disordered tetrafluoroborate ion rotates around the B(2)–F(5) bond; the three fluorine atoms split into two sets, indicating that the BF_4 ion takes alternative orientation randomly. Several bond angles and distances are thus unreasonable owing to this type of disorder. Possible hydrogen bonds are listed in Table V.[8] The interatomic distances outside the complex cation are given in Table VI.[8]

Figure 5 shows an ORTEP drawing of the complex cation and the numbering scheme of the atoms. The bond lengths and angles within the complex cation are given in Table VII and VIII.[8] The cobalt atom is surrounded by four nitrogen and two oxygen atoms at the apices of a slightly distorted octahedron. The average bond length of four Co–N bonds is 1.954 (1) Å, slightly longer than those of 1.948 (2) Å in complex II and 1.949 (3) Å in complex III. The bond angle of N(3)–Co–N(4) and the average angle subtended at the cobalt atom by the three chelate rings of the tren are smaller than those in the latter. These observations suggest that the tren coordinates more loosely to the cobalt atom than that in II and III. The chelate rings of tren (A, B, and C—labeled as in Figures 1 and 6) adopt flexible conformation, which is reflected in the disordered structure of A ring and the large thermal parameters of C(4) and C(6). The B and C rings adopt an envelope conformation, and they are λ and δ, respectively. In the ring A which has a conformational disorder, the planar conformation is predominant over the envelope one

Table II. Positional Parameters ($\times 10^5$ for Nonhydrogen Atoms, $\times 10^4$ for H) and Thermal Parameters ($Å^2 \times 10^3$ for U_{eq} or U_{iso})

	x	y	z	U_{eq}/ U_{iso}
Co	23091 (2)	15793 (1)	39963 (3)	37
C(1)	48471 (14)	19214 (6)	38413 (11)	69
C(2) ($G_1{}^a$)	39681 (39)	22578 (7)	40694 (92)	135
C(2′) ($G_2{}^a$)	40931 (26)	22090 (11)	48413 (31)	40
C(3)	42808 (21)	13711 (7)	19745 (21)	67
C(4)	34236 (42)	16168 (12)	9680 (8)	85
C(5)	45972 (5)	12135 (4)	48006 (8)	67
C(6)	40969 (21)	13292 (6)	63796 (23)	78
C(7)	10757 (9)	3912 (3)	35605 (21)	71
C(8)	9475 (12)	8389 (2)	37830 (29)	41
C(9)	−2829 (21)	10245 (1)	40715 (9)	41
C(10)	−3866 (12)	14371 (3)	43004 (10)	52
C(11)	−16828 (23)	16281 (5)	44982 (46)	97
C(12)	−14872 (10)	7680 (3)	42109 (11)	46
C(13)	−17840 (9)	6078 (4)	56377 (7)	58
C(14)	−29120 (6)	3656 (1)	58451 (8)	68
C(15)	−37068 (2)	2906 (1)	45929 (2)	66
C(16)	−34209 (12)	4584 (4)	30791 (11)	54
C(17)	−42679 (7)	3889 (5)	17779 (22)	68
C(18)	−40031 (8)	5504 (2)	4025 (11)	80
C(19)	−28743 (10)	7870 (4)	1575 (5)	71
C(20)	−20365 (20)	8531 (2)	13587 (21)	66
C(21)	−22855 (16)	6996 (4)	28721 (12)	48
N(1)	41639 (8)	15147 (1)	36102 (25)	44
N(2)	26775 (12)	21549 (1)	43317 (7)	46
N(3)	21282 (18)	16324 (2)	17226 (20)	66
N(4)	26894 (27)	14476 (6)	61945 (13)	54
O(1)	20425 (10)	10220 (1)	37043 (9)	46
O(2)	5544 (7)	16957 (1)	43568 (11)	56
O(3)	17555 (33)	22308 (7)	76380 (28)	160
O(4)	−1242 (10)	17317 (19)	87740 (26)	193
B(1)	15492 (12)	6920 (2)	89419 (15)	70
B(2)	15486 (16)	28476 (3)	11756 (19)	80
F(1)	27921 (11)	7539 (6)	91115 (16)	224
F(2)	10971 (2)	3448 (1)	92533 (3)	195
F(3)	9936 (5)	9802 (5)	97706 (30)	275
F(4)	13482 (21)	7488 (7)	75005 (39)	260
F(5)	24315 (45)	25809 (8)	10738 (17)	268
F(6) ($G_3{}^a$)	12619 (16)	29530 (8)	−2770 (23)	214
F(7) ($G_3{}^a$)	15867 (69)	31889 (12)	16327 (81)	243
F(8) ($G_3{}^a$)	8991 (37)	25731 (8)	18164 (68)	197
F(6′) ($G_3{}^a$)	2033 (18)	27973 (39)	9297 (15)	235
F(7′) ($G_3{}^a$)	21294 (50)	30509 (13)	2067 (20)	339
F(8′) ($G_3{}^a$)	15263 (85)	28895 (23)	26499 (30)	178
H(C1A)	5620 (4)	1914 (3)	4259 (6)	64 (3)
H(N2B)	2399 (15)	2240 (4)	5184 (12)	76 (7)
H(C3A)	5239 (12)	1401 (6)	1708 (29)	103 (6)
H(C3B)	4072 (8)	1073 (4)	2052 (35)	73 (5)
H(C4A)	3353 (14)	1504 (4)	46 (11)	60 (3)
H(C4B)	3668 (22)	1824 (9)	1011 (9)	87 (10)
H(N3A)	1406 (25)	1347 (4)	1543 (38)	114 (5)
H(N3B)	1718 (28)	1837 (13)	1321 (45)	106 (5)
H(C5A)	5470 (4)	1198 (2)	5128 (10)	76 (1)
H(C5B)	4339 (2)	952 (2)	4502 (3)	49 (1)
H(C6A)	4570 (15)	1533 (7)	6736 (31)	84 (10)
H(C6B)	3985 (29)	1073 (5)	7347 (19)	76 (7)
H(N4A)	2491 (20)	1646 (9)	6932 (9)	52 (2)
H(N4B)	2146 (29)	1184 (2)	6515 (29)	68 (9)
H(C7A)	859 (4)	309 (2)	4272 (6)	102 (2)
H(C7B)	761 (3)	279 (1)	2594 (10)	56 (1)
H(C7C)	1913 (9)	286 (2)	3228 (9)	79 (3)
H(C11A)	−1692 (15)	1789 (5)	5312 (9)	74 (4)
H(C11B)	−2221 (27)	1467 (9)	4352 (20)	105 (7)
H(C11C)	−1651 (18)	1827 (7)	4033 (12)	83 (7)
H(C13)	−1167 (15)	672 (3)	6613 (8)	58 (4)
H(C14)	−3057 (6)	232 (2)	6793 (8)	52 (2)
H(C15)	−4568 (1)	151 (1)	4653 (1)	63 (1)
H(C17)	−5184 (5)	208 (2)	1901 (5)	117 (1)
H(C18)	−4648 (4)	591 (2)	−142 (11)	67 (2)
H(C19)	−2579 (9)	867 (3)	−607 (8)	39 (2)
H(C20)	−1383 (12)	986 (4)	1477 (16)	62 (2)

[a] Population parameters of the disordered atoms: $G_1 = 0.61$ (11), $G_2 = 0.39$ (11), and $G_3 = 0.50$ (5).

Table VII. Bond Length (Å) and Angles (Deg) within the Complex Cation

Co–N(1)	1.948 (1)	Co–N(2)	1.962 (1)
Co–N(3)	1.948 (1)	Co–N(4)	1.957 (1)
Co–O(1)	1.880 (1)	Co–O(2)	1.871 (1)
N(1)–C(1)	1.530 (1)	C(1)–C(2)	1.447 (2)
C(1)–C(2′)	1.493 (2)	C(2)–N(2)	1.388 (3)
C(2′)–N(2)	1.530 (1)	C(8)–C(9)	1.428 (1)
C(9)–C(10)	1.383 (1)	C(8)–O(1)	1.281 (1)
C(10)–O(2)	1.293 (1)	C(9)–C(12)	1.506 (1)
C(12)–C(13)	1.358 (1)	C(13)–C(14)	1.421 (1)
C(14)–C(15)	1.364 (1)	C(15)–C(16)	1.431 (1)
N(1)–Co–N(2)	86.7 (1)	N(1)–Co–N(3)	86.4 (1)
N(1)–Co–N(4)	86.6 (1)	N(3)–Co–N(4)	170.1 (1)
O(1)–Co–O(2)	94.7 (1)	Co–N(1)–C(1)	109.4 (1)
N(1)–C(1)–C(2)	114.0 (3)	N(1)–C(1)–C(2′)	113.2 (2)
C(1)–C(2)–N(2)	115.5 (5)	C(1)–C(2′)–N(2)	105.0 (2)
Co–N(2)–C(2)	113.5 (3)	Co–N(2)–C(2′)	109.8 (2)
Co–O(1)–C(8)	125.8 (1)	Co–O(2)–C(10)	125.5 (1)
C(8)–C(9)–C(10)	121.1 (2)	C(8)–C(9)–C(12)	120.0 (2)
C(9)–C(12)–C(13)	113.4 (1)	C(10)–C(9)–C(12)	118.8 (2)
C(13)–C(12)–C(21)	121.5 (1)	C(9)–C(12)–C(21)	120.1 (1)
C(9)–C(8)–O(1)	125.8 (1)	C(9)–C(10)–O(2)	126.9 (1)

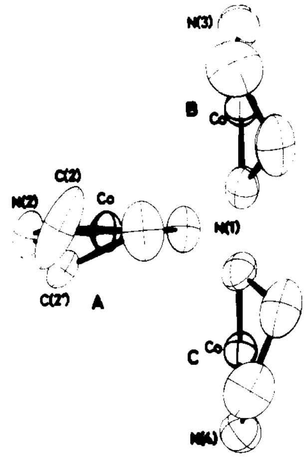

Figure 6. Conformation of the three chelate rings of tren.

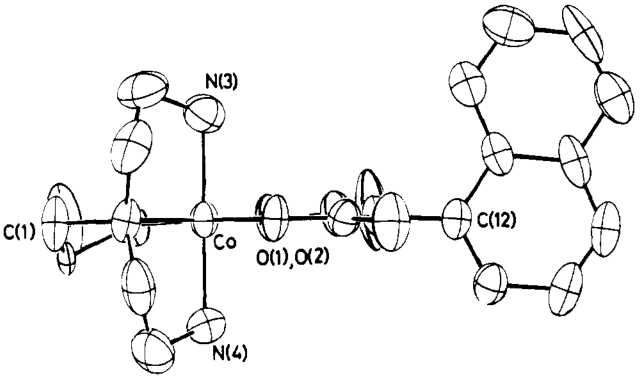

Figure 7. Projection of complex I along the line of O(1)–O(2).

by the ratio of 6:4. The interatomic distance of C(2)–N(2) is very short owing to large thermal parameters. Other bond distances and angles are normal.

The difference of the bond length in the two Co–O's of the acac ring is 0.009 (1) Å and is less than those in complexes II and III. A projection along the line through O(1) and O(2) is shown in Figure 7. The acac ring takes a planar structure in contrast to the 2,4-dinitro analogue. This fact supports authors' suggestion[3,4] that electrostatic interactions between the amino and *o*-nitro groups forced the acac ring to adopt a flattened boat form. The short axis of nathalene, C(12)··C(15), bends from the acac plane as if to keep benzo group away from the opposing amino group, its tilt angle being 5.6

(1)° to the least-squares plane of the acac ring.

Bond distance between the α and β carbons of the naphthalene ring are shorter than the β–β bonds observed in other naphthalene derivatives.[10] The naphthalene ring inclines slightly as the benzo group approaches N(2), and their dihedral angle is 87.6 (1)° to the least-squares plane of the acac ring. Since the inclination of the aromatic ring results in only a slight change in the direction of polarization, it seems to contribute little to the rotational strength of these complexes in the present series.[6]

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Supplementary Material Available: A listing of observed and calculated structure factors and tables of thermal parameters (Table III), observation of Bijvoet pairs (Table IV), possible hydrogen bonds (Table V), interatomic distances outside of the molecule (Table VI), nonessential bond lengths and angles (Table VIII) (24 pages). Ordering information is given on any current masthead page.

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[10] Harata, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2747. Ferraris, G.; John, D. W.; Yerkess, J.; Bartle, K. D. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1628 and literature cited in these references.

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Crystal Structure of the Axial (Orange-Yellow) Isomer of Bis(methyldiphenylphosphine)tetrakis(trifluoroacetato)dimolybdenum

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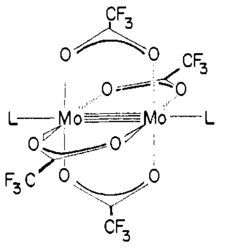
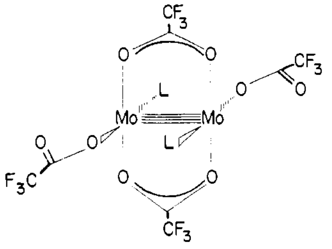
The X-ray crystal structure of the orange-yellow isomer of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ confirms that it possesses a class I (axial) structure as previously deduced spectroscopically. Accordingly, $PMePh_2$ is capable of forming both class I and class II (equatorial) adducts with $Mo_2(O_2CCF_3)_4$. NMR studies show that an equilibrium between the two isomers is established in solution. Crystal data: space group $P2_1/c$; $a = 9.923$ (1) Å, $b = 22.517$ (2) Å, $c = 18.735$ (3) Å, $\beta = 99.18$ (1)°; $V = 4132$ (2) Å^3; $Z = 4$; $R = 4.43\%$, $R_w = 6.63\%$; Mo–Mo = 2.128 (1) Å, Mo–P = 2.988 ± 0.024 Å, Mo–Mo–P = 166.15 ± 0.16°.

We have recently shown that tetrakis(trifluoroacetato)dimolybdenum yields 2:1 coordination complexes, $Mo_2(O_2CCF_3)_4(PR_3)_2$, with various tertiary phosphines.[1] Two general classes of complexes were isolated, referred to as class I and class II, as judged by infrared and NMR spectroscopy. Class I complexes were those in which the phosphine ligands were coordinated to axial sites (A), while class II complexes were those in which the phosphine ligands were coordinated to equatorial sites, one isomer of which is shown (B). On the basis of a cone angle vs. basicity graph, we showed that class II complexes were formed only by the smallest and most basic phosphines.[1]



A



B

A subsequent article has demonstrated that the crystal structures of $Mo_2(O_2CCF_3)_4(PPh_3)_2$ and $Mo_2(O_2CCF_3)_4(PEt_2Ph)_2$ are in complete accord with our findings, viz., that the former is a class I complex while the latter is a class II complex.[2] The structure of the latter is a testament to the predictive value of our cone angle and basicity criteria, since $Mo_2(O_2CCF_3)_4(PEt_2Ph)_2$ had not been previously prepared by us nor structurally characterized by spectroscopic studies.

In our original publication, we described the preparation of an orange-yellow complex, $Mo_2(O_2CCF_3)_4(PMePh_2)_2$, which was assigned a class I (axial) structure.[1] However, Cotton and Lay were unable to prepare this compound by our published method and instead synthesized a compound of the same stoichiometry by a different route. Its color was reported to be red-orange, and crystallographic analysis revealed a class II (equatorial) structure.[2]

Table I. Crystal Data

space group: $P2_1/c$	$V = 4132$ (2) Å^3
$a = 9.923$ (1) Å	$Z = 4$
$b = 22.517$ (2) Å	mol wt = 1044.38
$c = 18.735$ (3) Å	$d_{calcd} = 1.679$ g cm^{-3}
$\beta = 99.18$ (1)°	$\mu_{calcd} = 7.8$ cm^{-1}
$\alpha = \gamma = 90°$	size = 0.27 × 0.31 × 0.45 mm

diffractometer: Enraf-Nonius CAD-4
radiation: Mo K$\bar{\alpha}$, $\bar{\lambda} = 0.710\,73$ Å
monochromator: highly oriented graphite
scan range, type: $3 \leqslant 2\theta \leqslant 45°$, θ–2θ
scan speed, width: 0.6–6.7° min^{-1}, $\Delta\theta = (0.6 + 0.347 \tan \theta)°$
rflctns: 5926, 5393 unique, 4273 with $I > 3\sigma(I)$

$R = 4.43\%$	variables = 523
$R_w = 6.63\%$	GOF = 3.01

In view of this discrepancy, we have prepared $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ as originally described, with the exception that the solution volume was ca. 5 mL rather than ca. 10 mL. Herein we report its X-ray crystal structure and show that it is indeed a class I, axial diadduct. Some spectroscopic comparisons and preparative details involving the orange-yellow and red-orange isomers are also described.

Results and Discussion

An ORTEP[3] drawing of the orange-yellow isomer of $Mo_2(O_2CCF_3)_4(PMePh_2)_2$ (Figure 1) is that of a class I structure, as deduced previously by spectroscopic analysis.[1] Bond lengths and angles involving the molybdenum atoms are given in Table III. Most of the molecular features are quite normal, except for the large anisotropic thermal motion of the fluorine atoms

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[1] Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 805–810.

[2] Cotton, F. A.; Lay, D. G. *Inorg. Chem.* **1981**, *20*, 935–940.

[3] Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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