Table I. Coordinates and Thermal Parameters for [(4-Methylimidazole)pentaamminecobalt(III)] Trichloride Dihydrate (Numbering As in Ref 1)

atom	x	y	z	U_{eq}, Å$^{2\,a}$
Co	0.1556 (0.4)	$^1/_4$	0.0844 (0.8)	0.0261 (2)
Nh(1)	0.2231 (2)	$^1/_4$	−0.0416 (5)	0.0356 (12)
Nh(25)	0.1127 (2)	0.0485 (5)	−0.0119 (3)	0.0348 (8)
Nh(34)	0.1996 (2)	0.0500 (5)	0.1791 (3)	0.0353 (8)
N(3)	0.0899 (2)	$^1/_4$	0.2108 (5)	0.0309 (11)
C(4)	0.0983 (3)	$^1/_4$	0.3422 (6)	0.0401 (16)
C(5)	0.0413 (3)	$^1/_4$	0.3993 (6)	0.0399 (16)
M(5)	0.0234 (4)	$^1/_4$	0.5342 (7)	0.0609 (22)
N(1)	−0.0017 (2)	$^1/_4$	0.3025 (5)	0.0417 (14)
C(2)	0.0292 (3)	$^1/_4$	0.1923 (6)	0.0351 (15)
Cl(1)	0.2626 (0.8)	$^1/_4$	0.4467 (2)	0.0432 (4)
Cl(2)	0.4828 (0.8)	$^1/_4$	0.6381 (2)	0.0428 (4)
Cl(3)^b	0.3547 (1)	0.2004 (14)	0.1290 (3)	0.0922 (15)
W(1)	0.3684 (2)	$^1/_4$	0.8241 (5)	0.0543 (13)
W(2)^b	0.1643 (4)	0.1717 (24)	0.7102 (7)	0.1300 (47)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i^*a_j^*)(\vec{a}_i\cdot\vec{a}_j)]$; $\sigma(U_{eq}) = 6^{-1/2}\langle\sigma(U_{ii})/U_{ii}\rangle U_{eq}$. ^{b} Half-occupied sites.

Table II. Selected Distances (Å) and Angles (deg)

Co–Nh(1)	1.966 (5)	C(4)–C(5)	1.362 (9)
Co–Nh(25)	1.969 (3)	C(5)–N(1)	1.376 (8)
Co–Nh(34)	1.964 (4)	N(1)–C(2)	1.341 (8)
Co–N(3)	1.941 (5)	C(2)–N(3)	1.313 (8)
N(3)–C(4)	1.402 (8)	C(5)–M(5)	1.478 (10)

Nh(25)–Co–Nh(1)	89.6 (2)	Co–N(3)–C(4)	126.1 (4)
Nh(34)–Co–Nh(1)	89.6 (2)	Co–N(3)–C(2)	128.0 (4)
N(3)–Co–Nh(1)	179.1 (2)	N(3)–C(4)–C(5)	108.9 (5)
Nh(34)–Co–Nh(25)	88.6 (1)	C(4)–C(5)–N(1)	105.7 (6)
Nh(34)–Co–Nh(25)′	179.1 (1)	C(5)–N(1)–C(2)	108.4 (5)
N(3)–Co–Nh(25)	90.1 (2)	N(1)–C(2)–N(3)	111.1 (5)
N(3)–Co–Nh(34)	89.9 (2)	C(2)–N(3)–N(4)	105.9 (5)
Nh(25)–Co–Nh(25)′	91.7 (1)	C(4)–C(5)–M(5)	131.3 (6)
Nh(34)–Co–Nh(34)′	91.1 (1)	N(1)–C(5)–M(5)	123.0 (6)

but only serves to give a cosmetically better *R* index.

The final difference map shows maximum excursions of +1.23 and −1.16 e/Å^3, both in the $y = {}^1/_4$ plane, the first near Cl(3) and the second near the cobalt atom. It is clear that the model for Cl(3) and W(2) is unsatisfactory. There is a residual positive density running in a column along **b** where these atoms are located. In an attempt to model this better, I had placed Cl(3) and W(2) off the mirror plane, as disordered pairs of atoms. This led to a decrease in the U_{22}'s by 47% and 61%, respectively. These thermal parameters are still large, though: U_{22} for Cl(3) is 0.174 (11) Å^2 and for W(2) is 0.309 (33) Å^2, corresponding to mean deviations of 0.41 Å for Cl(3) and 0.56 Å for W(2) along **b**. It is possible[4] that in fact there is additional nonstoichiometric water in this column, perhaps one extra molecule every four or five cells. I did not develop a model for this. The remainder of the difference map is featureless but noisy.

In their discussion, HSA note that the plane of the imidazole ring is expected to make an angle of 45° with the Nh(1)–Nh(2)–Nh(4)–Co–N(3) plane. The expectation really is that the imidazole plane bisect the angles Nh(2)–Co–Nh(5) and Nh(3)–Co–Nh(4); because of the increased symmetry in the *Pnma* description, it now exactly does. The Nh(25)–Co–Nh(25)′ angle is 91.7 (1)°, so the angle between the imidazole planes and the Nh(25)–Co–Nh(1)–N(3) plane is 45.9 (1)°; for the Nh(34)–Co–Nh(34)′ angle of 91.1 (1)°, the interplanar angle is 45.6 (1)°.

On the basis of these refinements, I conclude that the structure of this cobalt compound is better described in the centric space group *Pnma*, rather than in *Pna*2$_1$. The addition of the mirror plane makes the molecule exactly planar; it improves the agreement of chemically equivalent distances, and it improves the overall pattern of thermal parameters. It is clear that the data are not good enough to allow refinement of all the hydrogen parameters, and even those that are well-behaved enough not to diverge lead to geometries that are unreasonable. I therefore believe the refinement with fixed hydrogen contributions based on hydrogen positions idealized from difference maps or calculated from known geometry is the best one. The coordinates, distances, and angles given in Tables I and II are from that refinement.

Acknowledgment. This work was supported in part by the Exxon Educational Foundation. I thank Richard E. Marsh for useful conversations.

Registry No. (4-Methylimidazole)pentaamminecobalt(III) trichloride dihydrate, 103203-21-0.

Supplementary Material Available: Tables of anisotropic thermal parameters and assigned hydrogen parameters (2 pages); a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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[4] Marsh, R. E., private communication.

Contribution from Chandlee Laboratory, Department of
Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802,
and Department of Chemistry, University of
Delaware, Newark, Delaware 19716

First Structurally Characterized Geometric Isomers of an Eight-Coordinate Complex. Structural Comparison between *cis*- and *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$

Ayusman Sen,*[1,2] Venkatasuryanarayana Chebolu,[1]
and Arnold L. Rheingold*[3]

Received October 5, 1986

Geometrical isomers should exist for eight-coordinate complexes;[4] however, none have been structurally characterized thus far. Indeed, it has been stated that "the preparation, isolation and characterization of such isomers remains an unanswered challenge".[5] Herein, we report the X-ray crystal structure of *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$ (**1**). This and the reported[6] structure of the corresponding trans isomer (**2**) constitute the first structural characterizations of a pair of geometrical isomers of an eight-coordinate complex. In addition, these are also the first geometrical isomers of a lanthanide-metal compound. Because of the spherical nature of the lanthanide ions and the absence of significant crystal field effects, the geometrical arrangement of ligands in lanthanide-metal complexes is normally governed by steric rather than bonding requirements.[7]

Results and Discussion

1 was obtained as a byproduct in low yield by the addition of diglyme to a mixture obtained by the reaction of SmI_2[8] with 2 equiv of *t*-BuOK. Interestingly, the addition of diglyme to $SmI_2(THF)_2$ alone resulted in the formation of the trans isomer (**2**).[6]

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(1) The Pennsylvania State University.
(2) Alfred P. Sloan Research Fellow, 1984-1988.
(3) University of Delaware.
(4) (a) Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179. (b) Lippard, S. J. *Prog. Inorg. Chem.* **1968**, *8*, 109.
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(6) Chebolu, V.; Whittle, R. R.; Sen, A. *Inorg. Chem.* **1985**, *24*, 3082.
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(8) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

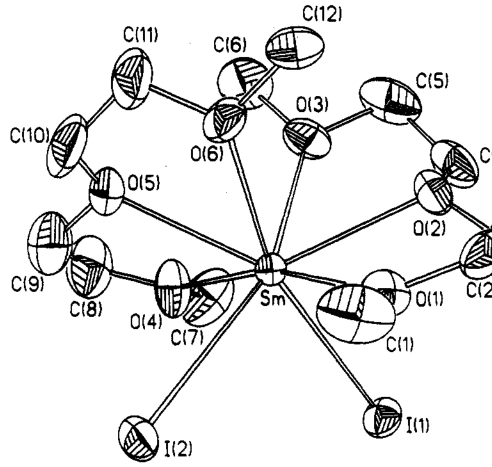

Figure 1. Structure and labeling scheme for *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$ (**1**). Hydrogen atoms are omitted, and thermal ellipsoids are at a 40% probability level.

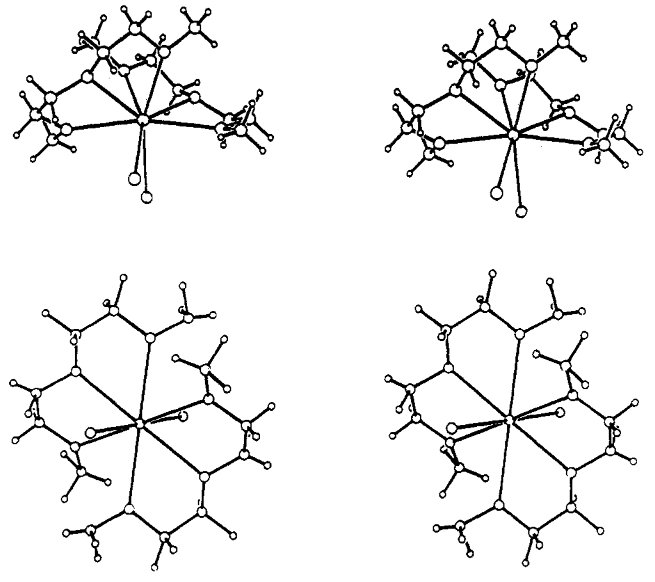

Figure 2. Stereoviews of the structures of *cis*- and *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$: **1** (top); **2** (bottom).

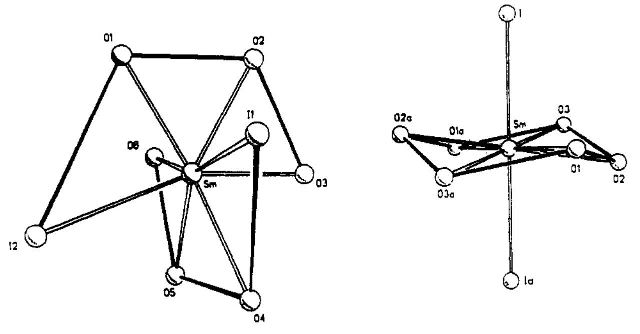

Figure 3. Coordination geometries for *cis*- and *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$: **1** (left); **2** (right). The solid construction lines emphasize the approximate dodecahedral structure of **1** and the axially bicapped trigonal antiprism structure for **2** (trianglar faces formed by O(1), O(3), O(2a) and O(2), O(1a), O(3a)).

Table I. Crystallographic Data for *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$

	(a) Crystal Data		
formula	$C_{12}H_{28}O_6SmI_2$	Z	8
cryst syst	orthorhombic	cryst dimens, mm	0.15 × 0.20 × 0.40
space group	*Pbca*	cryst color	deep red
a, Å	15.414 (5)[a]	μ(Mo Kα), cm^{-1}	55.7
b, Å	14.261 (3)	D(calcd), g cm^{-3}	2.045
c, Å	19.870 (6)	T_{max}/T_{min}	0.376/0.352
V, Å^3	4367.9 (20)	temp, K	295
	(b) Data Collection		
diffractometer	Nicolet R3	octants collcd	$+h,+k,+l$
radiation	Mo Kα (λ = 0.71073 Å)	reflcns collcd	3237
monochromator	graphite	no. of unique reflcns	2859
scan method	Wyckoff	no. of unique reflcns with $F_o \geq 5\sigma(F_o)$	1937
scan speed, deg min^{-1}	var, 5–20		
2θ limits, deg	$4 \leq 2\theta \leq 45$	std reflcns	3 std/97 reflcns (<2% var)
	(c) Structure Refinement		
R_F, % 3.85		data/parameter	10.1
R_{wF}, % 4.62		Δ/σ	0.08
GOF 0.97		highest peak (final diff map), e Å^{-3}	0.69

[a] Least-squares best fit, 25 reflections, $24° \leq 2\theta \leq 28°$.

1 crystallizes as discrete molecules without significant intermolecular contacts. Its structure and labeling scheme are shown in Figure 1. Figure 2 provides stereoviews of both **1** and **2** for comparison.

Choosing the most appropriate descriptor for eight-coordinate complexes is rarely straightforward—most descriptors are approximate because of the distortions present.[9] The choices for **2** are limited by the presence of the inversion center at Sm to three interrelated structures: hexagonal bipyramid (HB), axially bicapped trigonal antiprism (BTAP), or square prism (SP). SP is clearly wrong. The distortion in the equatorial plane for HB geometry is obvious in Figure 3; the average deviation of the oxygen atoms from a plane perpendicular to the I–Sm–I(a) axis is 0.32 Å.[10] On the other hand, the equatorial plane distortion is exactly that required for a BTAP structure. For the cis isomer (**1**) there are no crystallographically imposed restrictions on structural classification. The best choice is a distorted dodecahedron, the distortions arising primarily from the inequality of the Sm–I and Sm–O distances. If a dodecahedron is visualized as two perpendicular interpenetrating trapezoids, as shown in Figure 3, the angle relating the best-fit trapezoidal planes and the deviations of the atoms from these planes indicate the reliability of the choices. Although other sets of trapezoidal planes were considered, the pair shown produced the smallest atomic displacements from the plane (average deviation, 0.18 Å), and the angle between these planes is 90 (1)°.

The Sm–I distances in the cis isomer (**1**), 3.332(1) and 3.333 (1) Å, are significantly longer than that in the trans isomer (**2**), 3.265 (1) Å. Interestingly, the latter distance is close to that observed for the mutually trans iodines in $SmI_2(NCCMe_3)_2$, 3.260 (1) Å.[6] The Sm–O distances are slightly shorter in **1**, average 2.68 Å, compared to **2**, average 2.70 Å.

Experimental Section

The reagent grade solvents were appropriately dried and deoxygenated prior to their use. SmI_2 was synthesized by a published procedure.[8] All manipulations were carried out either on a high-vacuum line or in a N_2-filled drybox.

Synthesis of 1. A 3.0-g (5.5-mmol) sample of $SmI_2(THF)_2$ and 1.2 g (10.9 mmol) of *t*-BuOK were stirred together in 100 mL of benzene at 25 °C for 24 h. At the end of this period, the reaction mixture was filtered and a dark solid was isolated from the filtrate by evaporation of the solvent. This solid was redissolved in a minimum amount of THF, and 1 mL of diglyme was added to it. When the mixture was allowed to stand, dark brown crystals of *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$ (**1**) were obtained in less than 1% yield.

Structure Determination. A brick-shaped crystal of **1** was sealed in a capillary tube under nitrogen and was found to diffract moderately well. The space group was uniquely assigned from systematic absences. Crystallographic data for **1** are summarized in Table I. Data were

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(9) (a) Reference 4. (b) Burdett, J. K.; Hoffmann, R.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2553.

(10) For comparison, those few structures for which the HB structure has been claimed show deviations of less than 0.1 Å. For example, $UO_2(H_2O)_2(NO_3)_2$ has two independent molecules: (I) average deviation 0.02 Å; (II) average deviation 0.07 Å. Dalley, N. K.; Mueller, M. H.; Simonsen, S. H. *Inorg. Chem.* **1971**, *10*, 323.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$

	x	*y*	*z*	*U*[a]
I(1)	5987.5 (7)	2146.5 (8)	−355.0 (5)	59 (1)
I(2)	6454.9 (8)	4103.9 (8)	1569.5 (6)	70 (1)
Sm	4947.3 (4)	2575.7 (5)	1076.3 (3)	35 (1)
O(1)	4265 (6)	4143 (7)	538 (5)	61 (4)
O(2)	3611 (6)	2448 (8)	240 (5)	59 (4)
O(3)	3970 (7)	1038 (7)	1075 (6)	70 (4)
O(4)	5977 (7)	1158 (8)	1490 (6)	75 (5)
O(5)	5071 (7)	2114 (7)	2385 (5)	61 (4)
O(6)	3725 (7)	3142 (7)	1945 (5)	63 (4)
C(1)	4291 (11)	5047 (11)	832 (10)	96 (9)
C(2)	3580 (11)	4097 (11)	57 (8)	72 (7)
C(3)	3585 (11)	3161 (13)	−264 (8)	81 (8)
C(4)	3443 (11)	1512 (12)	10 (9)	83 (8)
C(5)	3260 (11)	928 (13)	602 (11)	99 (9)
C(6)	3858 (12)	420 (12)	1644 (10)	96 (9)
C(7)	6159 (14)	358 (14)	1099 (10)	111 (10)
C(8)	6187 (14)	1017 (15)	2160 (10)	112 (10)
C(9)	5892 (13)	1773 (13)	2571 (10)	101 (9)
C(10)	4656 (15)	2788 (15)	2823 (8)	98 (9)
C(11)	3805 (13)	2917 (15)	2626 (8)	93 (9)
C(12)	2854 (11)	3253 (18)	1754 (9)	119 (11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Distances and Angles for *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$

(a) Bond Distances (Å)

I(1)–Sm	3.322 (1)	I(2)–Sm	3.333 (1)
Sm–O(1)	2.692 (10)	Sm–O(2)	2.653 (9)
Sm–O(3)	2.660 (10)	Sm–O(4)	2.699 (11)
Sm–O(5)	2.689 (10)	Sm–O(6)	2.679 (10)
O(1)–C(1)	1.415 (19)	O(1)–C(2)	1.425 (19)
O(2)–C(3)	1.428 (20)	O(2)–C(4)	1.434 (20)
O(3)–C(5)	1.451 (22)	O(3)–C(6)	1.444 (21)
O(4)–C(7)	1.408 (23)	O(4)–C(8)	1.384 (22)
O(5)–C(9)	1.406 (22)	O(5)–C(10)	1.446 (22)
O(6)–C(11)	1.396 (20)	O(6)–C(12)	1.404 (20)
C(2)–C(3)	1.480 (24)	C(4)–C(5)	1.468 (26)
C(8)–C(9)	1.428 (28)	C(10)–C(11)	1.381 (29)

(b) Bond Angles (deg)

I(1)–Sm–I(2)	92.0 (1)	I(1)–Sm–O(1)	90.1 (2)
I(2)–Sm–O(1)	81.2 (2)	I(1)–Sm–O(2)	80.0 (2)
I(2)–Sm–O(2)	140.4 (2)	O(1)–Sm–O(2)	60.3 (3)
I(1)–Sm–O(3)	96.9 (2)	I(2)–Sm–O(3)	159.1 (2)
O(1)–Sm–O(3)	117.6 (3)	O(2)–Sm–O(3)	60.2 (3)
I(1)–Sm–O(4)	80.7 (2)	I(2)–Sm–O(4)	89.4 (2)
O(1)–Sm–O(4)	166.7 (3)	O(2)–Sm–O(4)	126.6 (3)
O(3)–Sm–O(4)	73.5 (3)	I(1)–Sm–O(5)	138.5 (2)
I(2)–Sm–O(5)	80.0 (2)	O(1)–Sm–O(5)	127.9 (3)
O(2)–Sm–O(5)	130.1 (3)	O(3)–Sm–O(5)	80.8 (3)
O(4)–Sm–O(5)	58.7 (3)	I(1)–Sm–O(6)	161.2 (2)
I(2)–Sm–O(6)	96.0 (2)	O(1)–Sm–O(6)	74.4 (3)
O(2)–Sm–O(6)	83.0 (3)	O(3)–Sm–O(6)	81.4 (3)
O(4)–Sm–O(6)	116.3 (3)	O(5)–Sm–O(6)	60.0 (3)
Sm–O(1)–C(1)	125.5 (10)	Sm–O(1)–O(2)	121.2 (8)
C(1)–O(1)–C(2)	109.9 (12)	Sm–O(2)–C(3)	114.4 (9)
Sm–O(2)–C(4)	113.8 (9)	C(3)–O(2)–C(4)	115.8 (12)
Sm–O(3)–C(5)	121.1 (9)	Sm–O(3)–C(6)	124.7 (9)
C(5)–O(3)–C(6)	110.6 (12)	Sm–O(4)–C(7)	123.8 (10)
Sm–O(4)–C(8)	122.6 (11)	C(7)–O(4)–C(8)	111.5 (14)
Sm–O(5)–C(9)	113.8 (9)	Sm–O(5)–C(10)	112.9 (9)
C(9)–O(5)–C(10)	118.0 (13)	Sm–O(6)–C(11)	119.5 (10)
Sm–O(6)–C(12)	122.1 (9)	C(11)–O(6)–C(12)	111.9 (13)
O(1)–C(2)–C(3)	109.1 (13)	O(2)–C(3)–C(2)	109.9 (13)
O(2)–C(4)–C(5)	108.0 (14)	O(3)–C(5)–C(4)	108.2 (14)
O(4)–C(8)–C(9)	111.5 (7)	O(5)–C(9)–C(8)	113.4 (16)
O(5)–C(10)–C(11)	109.7 (15)	O(6)–C(11)–C(10)	112.9 (15)

collected to the limit of availability. The intensity data were corrected for *Lp* effects and for absorption (empirical, ψ-scan, seven reflections, 252 data, six-parameter ellipsoid model).

The structure was solved by direct methods. All non-hydrogen atoms were refined with anistropic temperature factors. Hydrogen atom locations were idealized (d(C–H) = 0.96 Å) and updated as isotropic contributions. All computer programs were from the SHELXTL library (Version 5.1) distributed by the Nicolet Corp., Madison, WI.

Table II provides the atomic coordinates for **1**, and Table III the bond distances and angles. Additional data are available as supplementary material.

Acknowledgment. Support of this research through a grant from the National Science Foundation (No. CHE-8312380) to A.S. is gratefully acknowledged. The National Science Foundation also contributed funds for the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Stereoview of the unit cell packing for **1** (Figure S1) and tables of anisotropic thermal parameters (Table S1) and hydrogen atom coordinates (Table S2) for **1** (3 pages); a table of observed and calculated structure factors for **1** (Table S3) (11 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department, Monash University, Clayton, Victoria 3168, Australia, Chemistry Department, Imperial College of Science and Technology, London SW7 2AY, England, Chemistry Department, University of Tasmania, Hobart, Tasmania 7001, Australia, and Institut für Anorganische und Analytische Chemie, Albert-Ludwigs Universität, 7800 Freiburg, Federal Republic of Germany

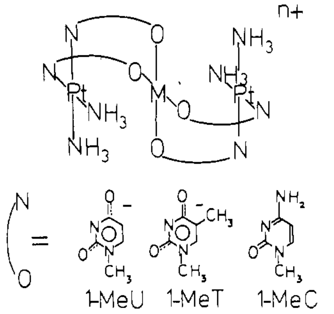
Magnetic Properties and Metal–Metal Interactions in Mixed-Metal (Pt_2M) Trimers (M = Ni, Co)

Darrell M. Duckworth,[†] David M. L. Goodgame,[‡] Michael A. Hitchman,*[§] Bernhard Lippert,[‖] and Keith S. Murray*[†]

Received November 7, 1986

Investigations of magnetic properties have often been used to provide information on the metal–metal interactions in polymeric transition-metal complexes.[1] This has almost always involved effects due to the coupling of the magnetic moments of paramagnetic metal ions, but the magnetic properties of some metal ions are quite sensitive to their ligand environment and this also has the potential to yield information on the effects that diamagnetic metal ions have on their paramagnetic neighbors in certain polymers. In particular, a recent study showed that the variation of the magnetic moments at low temperature caused by the zero-field splitting of the ground state can provide useful information about the nature of the ligand environment in low-symmetry Ni(II) complexes.[2]

As part of a general investigation of the ligating properties of pyrimidine nucleobases[3,4] we recently prepared a range of novel trimeric complexes of the form



where M = Cu(II), Ni(II), Co(II), Fe(II), and Mn(II). Here

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* To whom correspondence should be addressed.

[†] Monash University.

[‡] Imperial College of Science and Technology.

[§] University of Tasmania.

[‖] Albert-Ludwigs Universität.

0020-1669/87/1326-1823$01.50/0