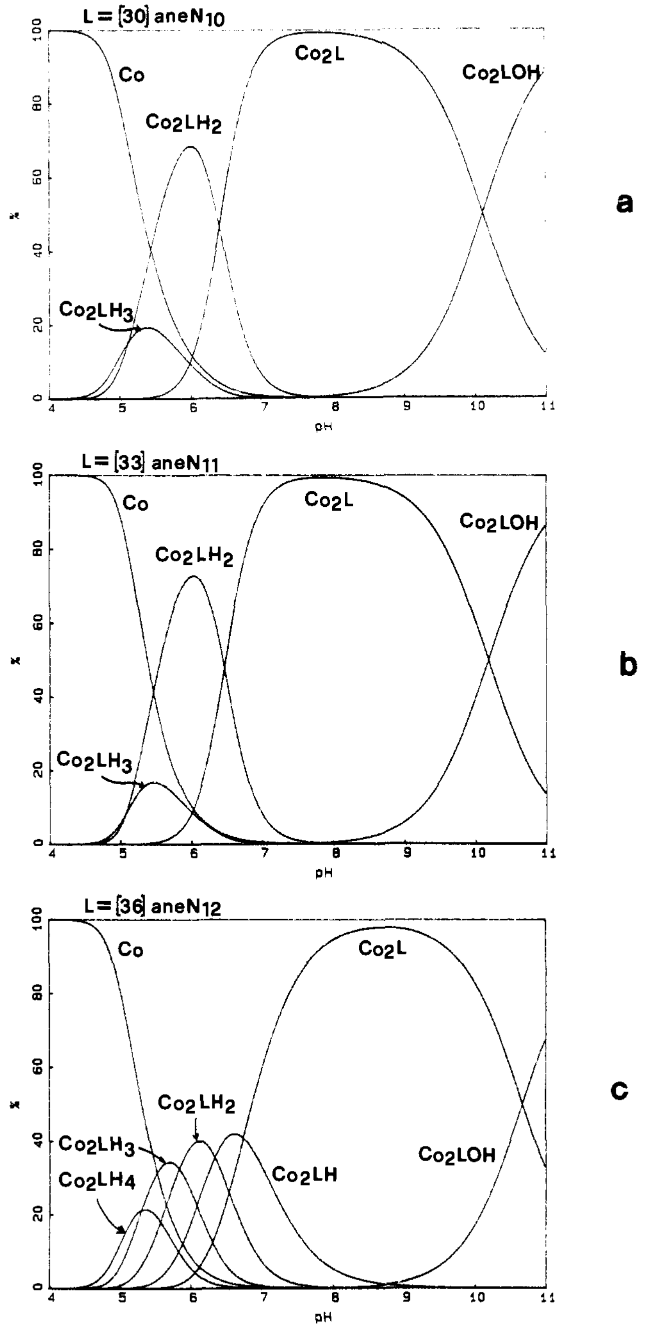

Figure 3. Calculated distribution of the equilibrium species in the systems (a) Co^{2+}/[30]aneN_{10}, (b) Co^{2+}/[33]aneN_{11}, and (c) Co^{2+}/[36]aneN_{12} in 0.15 mol dm^{-3} $NaClO_4$ solution at 25 °C for 2 × 10^{-3} mol dm^{-3} Co^{2+} and 10^{-3} mol dm^{-3} ligands.

is [27]aneN_9, while nickel(II),[10] zinc(II),[4] and cadmium(II)[2] also form dinuclear complexes with [24]aneN_8, and copper(II) forms dinuclear complexes even with [21]aneN_7.[5] The macrocycle [27]aneN_9 is able to form in solution both mononuclear and dinuclear cobalt(II) complexes. From the equilibrium data obtained for the system Co^{2+}/[27]aneN_9, the distribution of the complexes formed as a function of pH has been calculated for the 1:1 and 2:1 Co^{2+}: [27]aneN_9 molar ratios, and the results have been plotted in Figure 2. For the 1:1 molar ratio, only mononuclear cobalt(II) complexes are formed as the main species (Figure 2a), while when the ratio is 2:1, dinuclear cobalt(II) complexes become of major importance (Figure 2b). Notwithstanding, the ability of [27]aneN_9 to bind two cobalt(II) ions is not sufficiently large to prevent the presence of some free metal ion in alkaline solution (Figure 2b), and cobalt(II) hydroxide is formed as the pH is increased. For this reason the potentiometric measurements on this system were carried out without exceeding the 1.8:1 molar ratio. The dinucleating ability of large [3k]aneN_k ligands toward cobalt(II) ion increases from [27]aneN_9 to [30]aneN_{10}, [33]aneN_{11}, and [36]aneN_{12}, and only dinuclear cobalt(II) complexes are formed by the last three macrocycles (Figure 3). As shown in this figure, the species $[Co_2(L)]^{4+}$ (L = [30]aneN_{10}, [33]aneN_{11}, [36]aneN_{12}), is largely predominant over a rather wide pH range. This is a favorable condition for the study of O_2 uptake. From this point of view, [30]aneN_{10} seems to be the most promising ligand, yielding a dinuclear cobalt(II) complex in which two binding sites, one over each cobalt(II), could be available for coordination to molecular oxygen. [30]aneN_{10} and [33]aneN_{11} form triprotonated and diprotonated dinuclear cobalt(II) complexes in slightly acid solution (Figure 3a,b) while tetraprotonated to monoprotonated species are produced by the dinuclear complex of the largest macrocycle [36]aneN_{12} (Figure 3c). The $[Co_2(L)]^{4+}$ complexes are largely predominant from neutral to alkaline solution, and at higher pH values, hydroxy–dicobalt(II) species are formed (Figure 3). The stability constant related to the formation of the $[Co_2(L)]^{4+}$ species increases (Table I) from [27]aneN_9 to [36]aneN_{12}, as the number of nitrogen atoms in the macrocycles increases, in accord with an increasing number of donor atoms involved in the coordination to the two cobalt(II) ions. The stability constants for the $[Co_2(L)]^{4+}$ species are somewhat lower than those of the corresponding complexes of zinc(II), and the general trend of stability Co < Ni < Cu > Zn can be outlined for each macrocycle, comparing the results obtained in this and in previous studies.[2-10]

Registry No. [21]aneN_7, 296-85-5; [24]aneN_8, 297-11-0; [27]aneN_9, 57970-53-3; [30]aneN_{10}, 862-28-2; [33]aneN_{11}, 60464-68-8; [36]aneN_{12}, 24904-24-3.

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Molecular Structure of Hexakis(N,N'-diethylurea)manganese(II) Tetrabromomanganate(II)

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Received November 23, 1988

The absence of ligand field stabilization energy in high-spin manganese(II) complexes allows various coordination configurations. In previous report,[1] we described a pentacoordinated complex with monodentate ligands: dibromotris(N,N'-dimethylurea)manganese(II), with a distorted-bipyramidal structure having two bromine atoms in equatorial positions and the three dmu ligands (dmu = N,N'-dimethylurea) being oxygen bonded. Two axial dmu ligands are classically bonded with a Mn–O–C angle of 129.5°, whereas the equatorial dmu is unusually linearly bonded with a Mn–O–C angle of 180°. We report now the structure of a complex with the same stoichiometry, only with the dmu ligands replaced by N,N'-diethylurea (deu). From electronic spectra,[2] it was inferred that the compound was in fact an ionic mixed octahedral–tetrahedral complex: $[Mn(deu)_6][MnBr_4]$. The X-ray structure has now been solved and is reported here as well as a comparison with the $Mn(dmu)_3Br_2$ structure.

Experimental Section

Preparation of $Mn(deu)_3Br_2$. The preparation of $Mn(deu)_3Br_2$ (white powder) has been described previously.[2] Monocrystals were obtained by slow evaporation at room temperature in a desiccator of a concentrated solution of the complex in dry 1-butanol and ethanol (50/50). Small moisture-sensitive transparent prisms or diamond-shaped crystals were obtained after 1 month. Anal. Calcd for $MnC_{15}H_{36}N_6O_3Br_2$: C, 31.99;

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0020-1669/89/1328-2482$01.50/0

Table I. Crystallographic Data for $[Mn(deu)_6][MnBr_4]$

formula: $Mn_2C_{30}H_{72}N_{12}O_6Br_4$	fw: 1126.50
a = 19.247 (6) Å	space group: $P\bar{1}$
b = 13.095 (6) Å	T = 20 °C
c = 13.123 (9) Å	λ = 0.71069 Å
α = 118.53 (3)°	ρ_{obsd} = 1.396 g cm^{-3}
β = 109.23 (3)°	ρ_{calcd} = 1.392 g cm^{-3}
γ = 71.40 (4)°	μ = 37 cm^{-1}
V = 2687.8 Å^3	R_F = 0.092
Z = 2	R_{wF} = 0.075

Table II. Final Positional Parameters (×10^4) and Isotropic (or Isotropic Equivalent) Thermal Parameters[a] (×10^3 Å^2) for Non-Hydrogen Atoms in $[Mn(deu)_6][MnBr_4]$

	x	y	z	U (or U_{eq})
Br(1)	6522 (2)	1029 (3)	6382 (2)	123 (6)*
Br(2)	8627 (2)	1725 (3)	7422 (3)	169 (7)*
Br(3)	6896 (2)	3759 (3)	6099 (3)	199 (7)*
Br(4)	6977 (2)	3936 (3)	9317 (2)	116 (6)*
Mn(1)	7263 (2)	2588 (3)	7314 (3)	105 (8)*
Mn(2)	5000 (1)	0 (1)	0 (1)	130 (11)*
O(1)	4169 (11)	−762 (19)	65 (17)	148 (8)
C(1)	4076 (32)	−1396 (42)	508 (39)	192 (18)
N11)	3443 (20)	−1108 (31)	689 (27)	216 (16)
C(11)	2841 (23)	−41 (36)	775 (32)	199 (1)
C(13)	2210 (21)	−325 (33)	639 (32)	199 (1)
N(12)	4628 (25)	−2002 (38)	727 (35)	295 (24)
C(12)	4765 (22)	−2956 (37)	1006 (34)	199 (1)
C(14)	5517 (21)	−3147 (32)	1654 (32)	199 (1)
O(2)	4488 (14)	−286 (21)	−1827 (25)	185 (11)
C(2)	4093 (25)	−639 (33)	−2674 (41)	156 (15)
N(21)	3448 (19)	−955 (27)	−3284 (30)	211 (15)
C(21)	3054 (24)	−848 (34)	−2669 (35)	199 (1)
C(23)	2253 (21)	−691 (31)	−3286 (32)	199 (1)
N(22)	4478 (16)	−905 (22)	−3571 (25)	169 (11)
C(22)	5243 (23)	−763 (34)	−3468 (33)	199 (1)
C(24)	5668 (20)	−1792 (34)	−4229 (33)	199 (1)
O(3)	4145 (16)	1739 (29)	553 (27)	231 (15)
C(3)	4268 (23)	2588 (48)	1271 (45)	175 (16)
N31)	3394 (16)	3085 (25)	766 (26)	180 (11)
C(31)	2854 (22)	2750 (33)	−342 (37)	199 (1)
C(33)	2190 (20)	2856 (32)	−273 (32)	199 (1)
N(32)	4404 (21)	3568 (37)	2144 (36)	247 (18)
C(32)	5039 (25)	3740 (35)	2864 (37)	199 (1)
C(34)	5352 (20)	4630 (35)	3172 (32)	199 (1)
Mn(3)	0 (1)	5000 (1)	5000 (1)	79 (10)
O(4)	465 (9)	5506 (14)	3999 (14)	99 (6)
C(4)	955 (19)	5875 (31)	3873 (24)	116 (11)
N(41)	1626 (16)	5222 (25)	3755 (21)	162 (10)
C(41)	1675 (20)	3870 (37)	3318 (33)	199 (1)
C(43)	2379 (20)	3545 (34)	3562 (32)	199 (1)
N(42)	770 (14)	6914 (24)	3847 (20)	139 (9)
C(42)	93 (22)	8033 (34)	4243 (32)	199 (1)
C(44)	−336 (20)	7713 (33)	3254 (33)	199 (1)
O(5)	325 (10)	3129 (16)	3834 (15)	118 (6)
C(5)	901 (22)	2341 (35)	3999 (35)	147 (13)
N(51)	728 (12)	1247 (21)	3009 (21)	115 (8)
C(51)	98 (22)	1031 (32)	1849 (34)	199 (1)
C(53)	−420 (19)	899 (31)	2259 (32)	199 (1)
N(52)	1410 (15)	2352 (24)	4822 (24)	143 (10)
C(52)	2002 (22)	1414 (35)	4921 (34)	199 (1)
C(54)	2541 (19)	2021 (31)	6032 (33)	199 (1)
O(6)	1061 (8)	5023 (14)	6274 (16)	92 (5)
C(6)	1168 (17)	5440 (24)	7380 (29)	96 (10)
N(61)	1833 (13)	5799 (19)	7932 (20)	122 (8)
C(61)	2565 (21)	5481 (32)	7329 (33)	199 (1)
C(63)	2326 (20)	6453 (33)	7171 (32)	199 (1)
N(62)	759 (13)	5606 (18)	8018 (22)	113 (8)
C(62)	911 (20)	6129 (32)	9311 (36)	199 (1)
C(64)	196 (21)	6206 (31)	9584 (31)	199 (1)

[a] Starred values denote atoms refined anisotropically. The equivalent isotropic U value is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

H, 6.44; N, 14.92; Mn, 9.75; Br, 28.4. Found: C, 31.96; H, 6.54; N, 14.83; Mn, 9.8; Br, 28.5.

Table III. Relevant Interatomic Bond Lengths (Å) and Angles (deg) in $[Mn(deu)_6][MnBr_4]$ (with Esd's in Parentheses)

(1) Tetrahedral Manganese(II) Coordination			
Mn(1)–Br(1)	2.460 (6)	Mn(1)–Br(3)	2.508 (7)
Mn(1)–Br(2)	2.485 (5)	Mn(1)–Br(4)	2.493 (5)
Br(1)–Mn(1)–Br(2)	111.3 (2)	Br(2)–Mn(1)–Br(3)	106.8 (2)
Br(1)–Mn(1)–Br(3)	110.0 (2)	Br(2)–Mn(1)–Br(4)	111.9 (2)
Br(1)–Mn(1)–Br(4)	107.8 (2)	Br(3)–Mn(1)–Br(4)	108.9 (2)
(2) Octahedral Manganese(II) Coordination			
Mn(2)–O(1)	2.184 (28)		
Mn(2)–O(2)	2.165 (29)		
Mn(2)–O(3)	2.280 (28)		
Mn(3)–O(4)	2.226 (24)		
Mn(3)–O(5)	2.188 (16)		
Mn(3)–O(6)	2.170 (15)		
Mn(2)–O(1)–C(1)	143.4 (2)	Mn(3)–O(4)–C(4)	153.3 (2)
Mn(2)–O(2)–C(2)	154.0 (4)	Mn(3)–O(5)–C(5)	130.1 (2)
Mn(2)–O(3)–C(3)	125.5 (3)	Mn(3)–O(6)–C(6)	128.3 (2)
O(1)–C(1)	1.30 (6)	O(4)–C(4)	1.27 (5)
O(2)–C(2)	1.10 (6)	O(5)–C(5)	1.29 (5)
O(3)–C(3)	1.10 (7)	O(6)–C(6)	1.25 (4)
O(1)–C(1)–N(11)	112 (5)	O(4)–C(4)–N(41)	121 (3)
O(1)–C(1)–N(12)	112 (5)	O(4)–C(4)–N(42)	119 (3)
N(11)–C(1)–N(12)	136 (6)	N(41)–C(4)–N(42)	120 (3)
O(2)–C(2)–N(21)	151 (5)	O(5)–C(5)–N(51)	103 (3)
O(2)–C(2)–N(22)	105 (4)	O(5)–C(5)–N(52)	133 (4)
N(21)–C(2)–N(22)	104 (4)	N(51)–C(5)–N(52)	122 (4)
O(3)–C(3)–N(31)	83 (4)	O(6)–C(6)–N(61)	113 (3)
O(3)–C(3)–N(32)	177 (6)	O(6)–C(6)–N(62)	130 (3)
N(31)–C(3)–N(32)	97 (4)	N(61)–C(6)–N(62)	117 (3)

X-ray Structure Determination. A small prism was fixed in a sealed Lindemann glass capillary and mounted on a Philips PW 1100 automated diffractometer (monochromatic Mo K$\bar{\alpha}$ radiation source, λ = 0.71069 Å).

Cell constants were obtained from the least-squares refinement of 25 selected reflections with Philips software. Attempts to reduce the triclinic cell to a C monoclinic or a $\mathfrak{R}$ hexagonal cell failed. (The better refined C lattice would give α = 90.34 (3)° and γ = 90.14 (3)°.) This was confirmed by a careful examination of intensities that should have been equivalent.[3]

A total of 9747 independent reflections were recorded, of which 2142 were considered as observed ($I \geq 1.6\sigma(I)$).[4] Three standard reflections measured every 90 min (every 200 reflections) during the entire data collection showed no significant trend. Lorentz and polarization corrections were applied, but no absorption corrections were made. The transmission factor A ranged from 0.386 to 0.393 (0° < θ < 25°).

Normalized structure factors E were calculated, and classical tests[5] led unambiguously to the centrosymmetrical space group $P\bar{1}$. A Wilson plot gave an abnormally high average temperature factor, B = 7.75 Å^2.

The structure was solved by use of the Patterson technique (36 higher peaks) with the aid of direct methods (MULTAN).[6] After refinement of the heavy atoms (4 Br and 3 Mn), subsequent difference-Fourier maps[7] revealed non-hydrogen atoms, the positions of the terminal methyl carbons being the last found (some of their thermal parameters, reaching 16 Å^2, exhibit great thermal motion and disorder).

Full-matrix least-squares refinements minimizing $\sum w(\Delta F)^2$ with weight $w = 1.91/\sigma^2(F_o)$ converged to R = 0.092 and R_w = 0.075. Hydrogen atoms bonded to nitrogen atoms were introduced in idealized

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(3) Delaunay, J. Structures moléculaires et propriétés spectroscopiques de composés de coordination. Thèse d'Etat, Reims, France, 1985.

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(7) Preliminary crystallographic computations were performed on a local IBM 1130 computer with local programs derived from those of: Laing, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 1674. Final least-squares refinements in the full matrix were performed on a CII Honeywell-Bull computer (Gif sur Yvette, France) by using the SHELX program chain (Sheldrick, G. M. "SHELX-76-Program for Crystal Structure Determination and Refinement"; University of Cambridge: Cambridge, England, 1976). Because of limited refining parameters, three blocks were constituted by the three chemically distinguished entities Mn(1) + 4 Br, Mn(2) + 3 deu, Mn(3) + 3 deu.

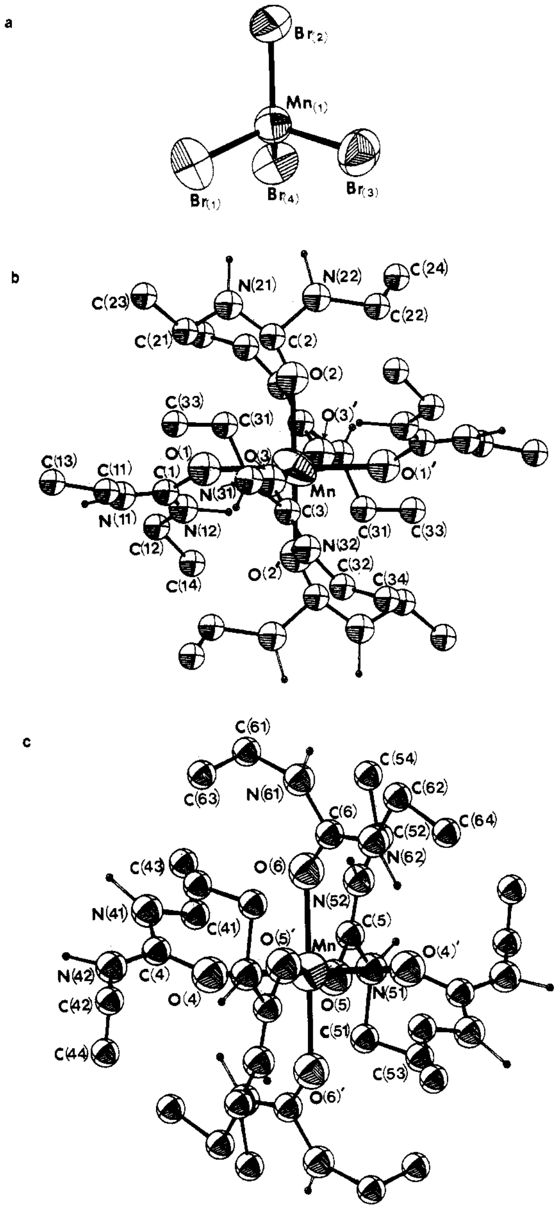

Figure 1. ORTEP model seen in perspective of the ionic mixed tetrahedral–octahedral $[Mn(deu)_6][MnBr_4]$ structure: (a) tetrahedral $[MnBr_4]^{2-}$; (b) octahedral coordination around Mn(2); (c) octahedral coordination around Mn(3).

positions (with the same isotropic thermal *B* value); those bonded to ethyl groups were not introduced.

A final difference map revealed no significant maxima, only very diffuse peaks (<0.61 e Å^{-3}) corresponding to the hydrogen atoms of the ethyl groups. Correlation matrix elements showed no peculiarity. The scattering factor and anomalous dispersion coefficients were taken from ref 8. Crystal and refinement data are summarized in Table I. Table II lists the final atomic coordinates and isotropic (or isotropic equivalent) thermal factors. Relevant geometric parameters are given in Table III.

Structural Results and Discussion

The molecular structure of the $Mn(deu)_3Br_2$ complex is shown in Figure 1. The ionic mixed octahedral–tetrahedral structure $[Mn(deu)_6][MnBr_4]$ is here ascertained.

The $[MnBr_4]^{2-}$ anion, located in a general position, is a distorted tetrahedron with Mn–Br bond lengths ranging from 2.460 (6) to 2.508 (7) Å and Br–Mn–Br angles ranging from 106.8 (2) to 111.9 (2)°. This departure from T_d symmetry is probably expanded by high thermal motions of the bromine atoms (highly pronounced anisotropy).

Two nonequivalent octahedral $[Mn(deu)_6]^{2+}$ cations are located on inversion centers. The octahedra are slightly distorted around the metal atom with O–Mn–O angles ranging from 84.7 (1.2) to 93.7 (0.6)°. The average Mn–O distance is 2.20 Å, as in other octahedral manganese(II) complexes with organic ligands.[9-11] The coordination mode of the deu molecules is classical (monodentate and angular), with Mn–O–C angles ranging from 125 to 154°, as in complexes of urea and its derivates.[12-18]

Geometrical comparisons can be made between the two analogous $[Mn(deu)_6][MnBr_4]$ (**1**) and $Mn(dmu)_3Br_2$ (**2**) complexes.

The Mn–Br distance found in tetrahedral $[MnBr_4]^{2-}$ (2.46–2.51 Å) is shorter than in the trigonal-bipyramidal environment in $Mn(dmu)_3Br_2$ (2.563 Å), itself shorter than those in octahedral Mn(II) complexes (2.59–2.74 Å).[19,20] This is consistent if only in regard to steric effect considerations.

The Mn–O distances seem to be more influenced by the bonding mode of the ligand than by the coordination number of the manganese(II): in **1**, they are 2.16–2.28 Å, similar to those found for axial dmu ligands in **2** (2.175 Å), with the same angular mode of coordination,[1] the oxygen atom sharing one lone pair with the metal atom.

Conformational comparisons of OCNN skeletons of the two ligands dmu and deu are interesting. In the pentacoordinated **2**, all dmu groups are planar[1] with the same syn,syn conformation[21] (in agreement with the assumed structure of the free ligand[22,23] whereas several conformations of deu are found in **1**: Only two have a syn,syn conformation, deu(2) and deu(4) (the numbers in parentheses correspond to those used in Table II and Figure 1); three others are rather syn,anti, deu(1), deu(5), and deu(6); the last deu(3) conformation is intermediate between syn,syn and syn,anti. Moreover, this last is the least planar and distorted enough; the deu molecules with a syn,anti conformation show the strongest deviation of the OCNN part from planarity, and several methyl groups rise out of the plane in any conformation.[3] Absence of the anti,anti conformation is noted, certainly avoided due to the steric bulk of ethyl groups.

Crystal packing in the unit cell of **1** is shown in the supplementary material. The packing is compact with only slight Br---H–N hydrogen bonds (3.43–3.57 Å). Other Br---N distances 3.77–3.82 Å) cannot be considered as hydrogen bonds according to the usual criteria.[24] Thus, in the bulky $[Mn(deu)_6]^{2+}$ cations, the free rotation of the terminal methyl groups is little hindered, whereas in $Mn(dmu)_3Br_2$ the molecules are linked together by a series of hydrogen bonds in a rather rigid net. This great freedom of motion in this structure is proved by an abnormally high overall

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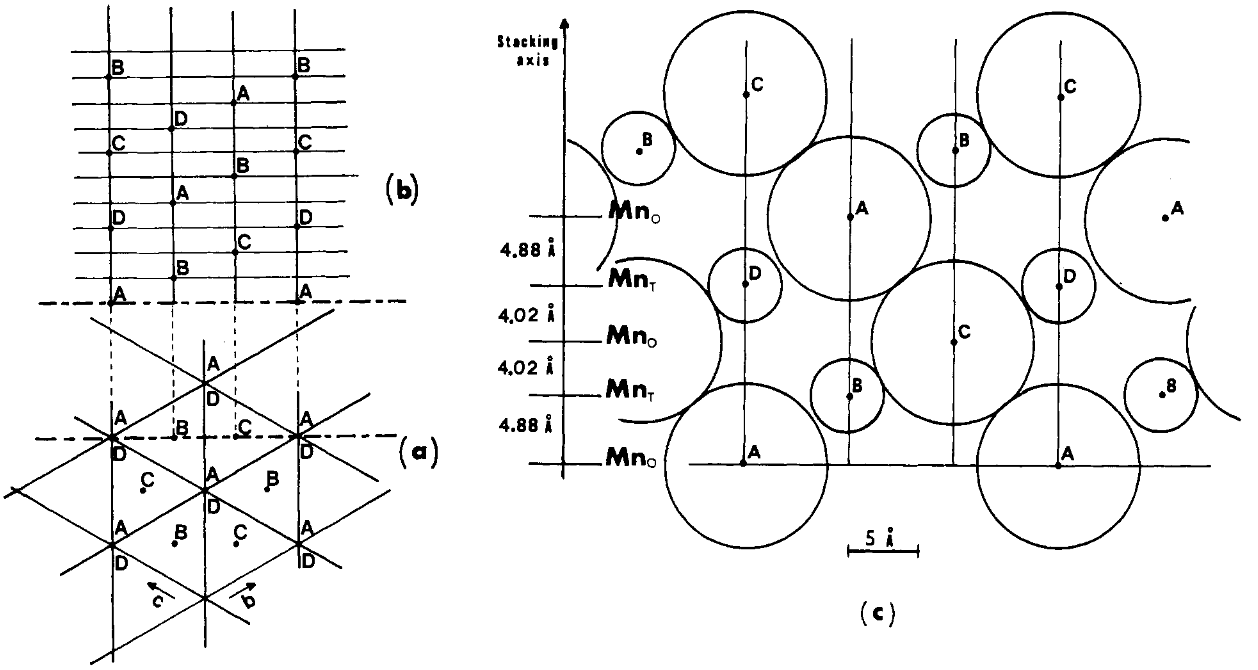

Figure 2. (a) Projection on the $(\vec{b},\vec{c})$ plane of centers of octahedral and tetrahedral spheres showing a like close-packed cubic arrangement (four successive levels only): (A and C) Mn_O, centers of octahedral spheres; (B and D) Mn_T, centers of tetrahedral spheres. (b) Elevation showing the layers (horizontal lines) viewed in the stacking direction. (c) Scale drawing of sphere layers along the stacking axis.

structure thermal parameter B (especially for ethyl carbons).

Moreover, considering the tetrahedral and octahedral groups as two kinds of spheres (with radii of about 2.5 and 6 Å, respectively), we studied the stacking of this ionic structure. From a projection on the $(\vec{b},\vec{c})$ plane of the central manganese atoms (of any sort), it can be described as a close-packed cubic structure, with staggered octahedral (Mn_O) and tetrahedral Mn_T) sphere layers. These are schematized in Figure 2a,b. It is worth noting that the densest possible packing is carried out, as sequences of bulky ACAC spheres in contact on the one hand and alternative bulky cations and smaller anions ABCD on the other hand. Octahedral and tetrahedral sphere layers along the stacking axis are separated by 4.88 and 4.02 Å, as shown in Figure 2c.

In conclusion, we have confirmation of a rare mixed tetrahedral–octahedral structure, which, to our knowledge, has not been previously reported in Mn(II) complexes. From powder patterns, the complex $[Mn(deu)_6][MnCl_4]$ is assumed to be isostructural.

Various conformations in the same complex have only been reported for Co(II) and Ni(II).[25,26] Hitherto, geometrical data on the tetrahedral $[MnBr_4]^{2-}$ anion were unknown, as in other transition-metal tetrabromides; in contrast, several were known for $[MCl_4]^{2-}$ (M = Ni(II), Co(II), Zn(II), Cu(II)[27-33] and the Mn–Cl distance in $[MnCl_4]^{2-}$ was just approximately given.[34] From all these structural results and thermodynamic ones,[35] we could attribute to Mn–Br a bond energy of ca. 560 kJ mol^{-1}.[3]

On the other hand, the destruction of planarity in deu molecules (when two CH_3 groups are added in chain ends of dmu) seems to hinder a trigonal-bipyramidal environment,[1] and moreover the bulkier $[Mn(deu)_6]^{2+}$ cation stabilizes the $[MnBr_4]^{2-}$ anion whereas $[Mn(dmu)_6]^{2+}$ does not;[3] however, these two octahedral cations exist, associated with iodide and perchlorate anions.[2,36]

Acknowledgment. We thank Dr Cl. Pascard (Gif-Sur-Yvette, France) for the use of the automated diffractometer and Dr J. Guilhem (Gif-sur-Yvette, France) for assistance in structure refinement.

Registry No. $[Mn(deu)_6]^{2+}[MnBr_4]^{2-}$, 41586-60-1.

Supplementary Material Available: A perspective view of packing in the unit cell and tables of all crystal data and collection parameters, anisotropic thermal parameters and root-mean-square displacements of heavy atoms, fractional coordinates of hydrogen atoms, hydrogen bonds and intermolecular contacts with principal angles between $[Mn(deu)_6][MnBr_4]$ asymmetric units, least-squares planes of the OCNN urea skeleton, dihedral angles giving *N,N'*-diethylurea conformations, and lattice spacings for $[Mn(deu)_6][MnX_4]$ (X = Br, Cl) (8 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of a New Polymorph of Tungsten(VI) Sulfide Tetrachloride, $WSCl_4$

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Received January 17, 1989

Interest in tungsten(VI) tetrahalide oxides and chalcogenides stems in part from their versatility as starting materials for synthesis[1] as well as from curiosity concerning the diverse structural forms that they adopt. Infrared data indicate that the

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