Synthesis and Magnetic Susceptibility of Novel Types of Bimetallic, Octanuclear, Cubane-Structured Complex Ions Containing Molybdenum(VI)/Tungsten(VI) and Chromium(III)/Cobalt(III). Crystal Structure of {[MoO₄Cr(bispictn)]₄}(ClO₄)₄ · 3H₂O

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The synthesis, spectroscopic and magnetic properties of a novel type of bimetallic, cubane-structured complexes containing cores of $Mo^{VI}_4O_8^{8+}$ or $W^{VI}_4O_8^{8+}$ are described. The crystal structure of {[MoO₄Crbispictn]₄}(ClO₄)₄·3H₂O where bispictn = N,N'-bis(2-bipyridylmethyl)-1,3-propanediammine, $C_{15}H_{20}N_4$, has been determined from X-ray diffraction data. The complex crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions a = 14.572(9), b = 17.847(11), c = 19.548(11) Å, α = 104.03(3), β = 99.58(3) and γ = 112.50(2)°. The structure was refined to a final R-value of 0.098 for 3631 independent intensities. The cation has approximate 4 (S_4) symmetry and is built up about a distorted cube of molybedenum and oxygen atoms. The configurations at the chromium atoms are alternately Δ or Λ; the ligands bind to them in the cis-β form, so the complex is the Δ(β)(SS′)Λ(β)(RR′)-Λ(β)(SS′)Λ(β)(RR′) isomer. The magnetic susceptibilities of the chromium complexes have been measured. The antiferromagnetic coupling between neighbouring chromium(III) ions gives J = 14.5 cm⁻¹ in the molybdenum complex, compared with 9.5 cm⁻¹ in the tungsten complex. A model is put forward in which this difference is related to the higher electron affinity of molybdenum(VI) compared to tungsten(VI).

There is continuing interest in compounds containing molybdenum arranged in a cubanoid core. This is partly because of the involvement of such species in important biological processes, and also because they are models for metal oxide surfaces acting as heterogeneous catalysts for organic transformations. We report here the synthesis of a novel type of octanuclear, bimetallic complex, {[Mo/WO₄Cr/Cobispictn]₄}(ClO₄)₄·nH₂O, with $Mo^{VI}_4O_8^{8+}$ or $W^{VI}_4O_8^{8+}$ as central, cubanoid cores surrounded by four bridging entities of [O₂Crbispictn]⁻ or [O₂Cobispictn]⁻ (Fig. 1). The ligand bispictn on the trivalent metal is the tetradentate amine ligand N,N'-bis(2-pyridylmethyl)-1,3-propanediamine (Fig. 2). Octanuclear, bimetallic cubanoid complexes, [Mo^VIO₄M^IIICp]₄·nH₂O, with M representing Rh or Ir and Cp representing C₅Me₅, have been described before, but the trivalent metals were arranged differently, resulting in a triple cubane framework.[1]

In forthcoming publications we will report how other amine ligands on chromium give rise to a totally different type of heteronuclear compound.
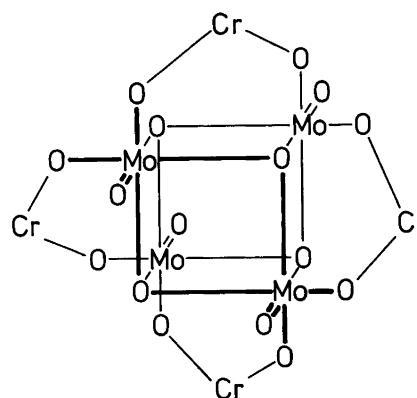
Fig. 1. A stylized depiction of the cubane framework in {[Mo^VIO₄Cr^IIIbispictn]₄}(ClO₄)₄·nH₂O. Mo^VI and Cr^III can be replaced by W^VI and Co^III, respectively. The ligand bispictn is omitted for clarity.
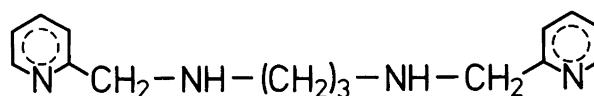

Fig. 2. N,N'-Bis(2-pyridylmethyl)-1,3-propanediamine, bispictn.

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Experimental

Reagents. $(NH_4)_2[MoOCl_5] \cdot H_2O$, $(NH_4)_2MoCl_5(H_2O)]$, $2HCl \cdot [Mo_6Cl_8]Cl_4 \cdot 8H_2O$ and K_2WCl_6 were prepared according to methods described in the literature.[2-5] The preparations of *cis*-β-[Crbispictn(OH)(H_2O)](ClO_4)_2·2H_2O and *cis*-β-[Cobispictn(OH)(H_2O)](ClO_4)_2·2H_2O have been published previously,[6] and *cis*-β-[Crbispictn(OH)(H_2O)]-I_2·2H_2O was prepared exactly as the corresponding perchlorate, except that sodium perchlorate was replaced by sodium iodide. All other chemicals were of reagent grade and were used without further purification.

Analyses. The chromium and cobalt analyses were performed on a Perkin-Elmer 403 atomic absorption spectrophotometer. The contents of molybdenum and tungsten were determined by spectrophotometric methods involving the thiocyanato complexes. The carbon, nitrogen, hydrogen and halogen analyses were carried out at the microanalytical laboratory of the H. C. Ørsted Institute using standard methods.

Optical spectroscopy. Electronic absorption spectra were recorded with a Perkin-Elmer Lambda 17 spectrophotometer. The spectra are characterized by their maxima (λ, ε), where λ is in nm and the molar absorption coefficient ε is in units of $1 \text{ mol}^{-1} \text{ cm}^{-1}$. The compounds were dissolved in water and *N*-methylformamide, respectively.

Magnetic susceptibility measurements. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 2–300 K at a field strength of 1.3 T. The susceptibility data have been corrected for diamagnetism by Pascal's constants. A more detailed description of the equipment is published elsewhere.[7,8]

X-Ray powder photographs. These were obtained on a camera of the Guinier type with Cu*K*α radiation. Silicon was used as a standard.

Preparations. Caution: Most of the described compounds are isolated as perchlorate salts and should be handled as potentially explosive compounds.

1. {[MoO_4Crbispictn]_4}(ClO_4)_4·6H_2O. [Crbispictn(OH)-(H_2O)](ClO_4)_2·2H_2O (0.231 g, 0.40 mmol) was dissolved in a solution of sodium hydroxide (4 ml, 0.1 M). $(NH_4)_2[MoOCl_5]\cdot H_2O$ (0.068 g, 0.20 mmol) was added slowly and the pH was adjusted to 8–8.5 by means of a solution of sodium hydroxide (2 M). A stoppered flask with the mixture was set aside for one week. By then, the muddy suspension had been transformed into a clear solution with shiny, red crystals. The crystals were filtered and washed with a solution of sodium perchlorate (1 M) and ethanol (75 %). Yield: 0.097 g (82 %). Anal. Calcd. for {[MoO_4Cr(C_15H_20N_4)]_4}(ClO_4)_4·6H_2O: Mo 16.13, Cr 8.74,

C 30.29, H 3.90, N 9.42, Cl 5.96. Found: Mo 16.06, Cr 8.60, C 30.33, H 3.55, N 9.44, Cl 6.70.

Exactly the same compound could be synthesized by an identical procedure from compounds containing molybdenum in lower oxidation states such as $(NH_4)_2[MoCl_5(H_2O)]$ or $2HCl \cdot [Mo_6Cl_8]Cl_4 \cdot 8H_2O$. In both cases the yields were considerably lower, but the crystals were larger and more suitable for structure determination.

2. {[MoO_4Crbispictn]_4}I_4·10H_2O was prepared exactly as described for 1, but from [Crbispictn(OH)(H_2O)]I_2·2H_2O (0.253 g, 0.40 mmol). Yield: 0.062 g (48 %). Anal. Calcd. for {[MoO_4Cr(C_15H_20N_4)]_4}I_4·10H_2O: Mo 14.99, Cr 8.12, C 28.14, H 3.94, N 8.75, I 19.82. Found: Mo 15.34, Cr 8.22, C 28.10, H 3.41, N 8.72, I 19.55.

3. {[MoO_4Cobispictn]_4}(ClO_4)_4·6H_2O was prepared exactly as described for 1, but from [Cobispictn(OH)(H_2O)]-(ClO_4)_2·2H_2O (0.234 g, 0.40 mmol). Yield: 0.088 g (74 %). Anal. Calcd. for [MoO_4Co(C_15H_20N_4)]_4(ClO_4)_4·6H_2O: Mo 15.94, Co 9.79, C 29.94, H 3.85, N 9.31, Cl 5.89. Found: Mo 16.08, Cr 9.77, C 29.77, H 3.46, N 9.25, Cl 6.23.

Table 1. {[MoO_4Crbispictn]_4}(ClO_4)_4·3H_2O crystal data.

Formula weight/g mol^{-1}	2324.9
Space group	*P*1̄
Cell parameters (295 K):	
a/Å	14.572(9)
b/Å	17.847(11)
c/Å	19.548(11)
a/°	104.03(3)
b/°	99.58(3)
c/°	112.50(2)
V/Å^3	4362(5)
No. of reflexions centred	4×25
2θ range	9.5–10.7
Calculated density (295 K) g cm^{-3}	1.770
Molecules per cell	2
Crystal size/mm^3	0.56×0.88×0.18
Developed forms	{001} {110} {01̄1}
Radiation (Mo*K*α) λ/Å	0.710 73
Filter	Nb
Linear absorption coefficient, μ/cm^{-1}	12.22
Range of transmission factors	0.532–0.800
Scan type	ω–2θ
ω-scan width, Δθ/°	1.2
No. of steps	50
Time per step/s	1
θ limits/°	1–20
Octants collected	*h*±*k*±*l*
Standard reflexions	2 2 0,4 2 1
Fall-off in intensity/%	<1
No. of unique data	8082
No. of data with $I/\sigma(I) > 3.0$	3631
No. of variables	534
Weights $w^{-1} = [\sigma_{cs}(F^2) + 1.03F^2]^{\frac{1}{2}} - |F|$	
$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$	0.098
$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$	0.110
S	2.58
Δ/σ_{max}	0.15
$\Delta\varrho_{max}/e$ Å^{-3}	1.5(2)

Table 2. {[MoO$_4$Crbispictn]$_4$}(ClO$_4$)$_4$·3H$_2$O, fractional coordinates and U_{eq}^a/U_{iso} (in Å^2).

Atom	x	y	z	U	Atom	x	y	z	U
Mo(1)	0.0672(3)	0.2041(2)	0.2052(2)	0.043(3)	C(301)	0.465(3)	0.647(2)	0.569(2)	0.053(13)
Mo(2)	0.0455(3)	0.3774(2)	0.1682(2)	0.042(3)	C(302)	0.556(3)	0.741(3)	0.604(2)	0.059(13)
Mo(3)	0.2590(3)	0.3904(2)	0.2903(2)	0.040(3)	C(303)	0.564(3)	0.789(3)	0.564(2)	0.059(13)
Mo(4)	0.0233(3)	0.3593(2)	0.3237(2)	0.042(3)	C(304)	0.497(3)	0.768(3)	0.493(2)	0.061(13)
Cr(1)	−0.0967(5)	0.1697(4)	0.0358(3)	0.046(5)	C(305)	0.408(3)	0.677(3)	0.465(2)	0.057(13)
Cr(2)	0.2970(5)	0.4944(4)	0.1588(3)	0.041(4)	N(31)	0.399(2)	0.623(2)	0.504(2)	0.041(9)
Cr(3)	0.2575(5)	0.5169(4)	0.4578(3)	0.044(5)	C(306)	0.330(3)	0.646(2)	0.388(2)	0.044(12)
Cr(4)	−0.0661(5)	0.1513(4)	0.3344(3)	0.044(5)	N(32)	0.231(2)	0.586(2)	0.391(1)	0.037(9)
O(1)	−0.022(2)	0.294(1)	0.216(1)	0.042(7)	C(307)	0.158(3)	0.628(2)	0.403(2)	0.054(13)
O(2)	0.118(2)	0.428(1)	0.276(1)	0.034(7)	C(308)	0.171(3)	0.664(3)	0.489(2)	0.064(14)
O(3)	0.158(2)	0.316(1)	0.186(1)	0.047(8)	C(309)	0.142(3)	0.600(3)	0.532(2)	0.069(14)
O(4)	0.136(2)	0.299(1)	0.307(1)	0.037(7)	N(33)	0.217(2)	0.568(2)	0.546(1)	0.043(9)
O(5)	0.151(2)	0.163(1)	0.209(1)	0.041(7)	C(310)	0.163(3)	0.497(3)	0.578(2)	0.052(13)
O(6)	−0.031(2)	0.424(1)	0.170(1)	0.046(8)	C(311)	0.238(3)	0.458(3)	0.581(2)	0.063(14)
O(7)	0.334(2)	0.345(1)	0.288(1)	0.041(7)	C(312)	0.246(3)	0.412(2)	0.631(2)	0.033(11)
O(8)	−0.054(2)	0.405(1)	0.318(1)	0.037(7)	C(313)	0.308(3)	0.376(2)	0.629(2)	0.042(12)
O(9)	−0.010(2)	0.155(1)	0.110(1)	0.037(7)	C(314)	0.364(3)	0.375(3)	0.576(2)	0.062(14)
O(10)	−0.018(2)	0.292(1)	0.079(1)	0.052(8)	C(315)	0.354(3)	0.423(3)	0.528(2)	0.056(13)
O(11)	0.320(2)	0.475(1)	0.247(1)	0.044(7)	N(34)	0.290(2)	0.460(2)	0.527(2)	0.039(9)
O(12)	0.150(2)	0.448(1)	0.143(1)	0.039(7)	C(401)	−0.180(3)	0.121(2)	0.456(2)	0.052(13)
O(13)	0.118(2)	0.427(1)	0.413(1)	0.045(8)	C(402)	−0.178(4)	0.126(3)	0.527(3)	0.074(15)
O(14)	0.298(2)	0.459(1)	0.384(1)	0.028(6)	C(403)	−0.086(4)	0.166(3)	0.584(2)	0.080(16)
O(15)	−0.028(2)	0.142(1)	0.249(1)	0.039(7)	C(404)	−0.001(4)	0.199(3)	0.567(3)	0.077(15)
O(16)	−0.047(2)	0.265(1)	0.347(1)	0.029(7)	C(405)	−0.003(3)	0.190(3)	0.495(2)	0.061(14)
C(101)	−0.202(3)	−0.014(2)	−0.073(2)	0.050(12)	N(41)	−0.086(3)	0.161(2)	0.438(2)	0.049(10)
C(102)	−0.298(3)	−0.107(2)	−0.102(2)	0.048(12)	C(406)	0.099(3)	0.232(2)	0.470(2)	0.065(14)
C(103)	−0.364(3)	−0.123(3)	−0.060(2)	0.069(14)	N(42)	0.089(2)	0.192(2)	0.391(2)	0.041(9)
C(104)	−0.358(3)	−0.062(2)	0.007(2)	0.051(13)	C(407)	0.140(3)	0.137(2)	0.382(2)	0.038(11)
C(105)	−0.267(3)	0.023(3)	0.029(2)	0.060(13)	C(408)	0.076(3)	0.046(2)	0.382(2)	0.044(12)
N(11)	−0.200(2)	0.040(2)	−0.011(2)	0.050(10)	C(409)	−0.020(3)	−0.006(2)	0.310(2)	0.041(11)
C(106)	−0.247(3)	0.083(3)	0.104(2)	0.057(13)	N(43)	−0.104(2)	0.025(2)	0.320(1)	0.040(9)
N(12)	−0.201(2)	0.174(2)	0.096(1)	0.037(9)	C(410)	−0.196(3)	−0.029(2)	0.251(2)	0.051(12)
C(107)	−0.269(3)	0,209(2)	0.083(2)	0.045(12)	C(411)	−0.276(3)	0.010(3)	0.254(2)	0.054(13)
C(108)	−0.316(3)	0.187(3)	−0.004(2)	0.062(13)	C(412)	−0.379(3)	−0.033(2)	0.223(2)	0.036(11)
C(109)	−0.237(3)	0.232(2)	−0.041(2)	0.050(12)	C(413)	−0.433(3)	0.012(3)	0.225(2)	0.052(13)
N(13)	−0.176(2)	0.182(2)	−0.056(2)	0.048(10)	C(414)	−0.395(3)	0.102(3)	0.255(2)	0.066(14)
C(110)	−0.090(3)	0.235(2)	−0.086(2)	0.052(12)	C(415)	−0.285(3)	0.140(3)	0.283(2)	0.057(13)
C(111)	−0.025(3)	0.197(3)	−0.089(2)	0.058(13)	N(44)	−0.223(2)	0.102(2)	0.284(2)	0.050(10)
C(112)	0.037(3)	0.198(2)	−0.136(2)	0.049(12)	Cl(1)	0.435(1)	0.270(1)	−0.085(1)	0.083(4)
C(113)	0.105(3)	0.164(3)	−0.132(2)	0.066(14)	O(17)	0.506(3)	0.251(2)	−0.116(2)	0.133(14)
C(114)	0.126(3)	0.128(2)	−0.078(2)	0.056(13)	O(18)	0.476(3)	0.272(3)	−0.011(2)	0.171(17)
C(115)	0.054(3)	0.128(2)	−0.029(2)	0.051(13)	O(19)	0.444(3)	0.355(2)	−0.074(2)	0.114(12)
N(14)	−0.011(2)	0.158(2)	−0.038(2)	0.048(10)	O(20)	0.337(5)	0.216(4)	−0.111(3)	0.264(27)
C(201)	0.282(3)	0.572(2)	0.034(2)	0.047(12)	Cl(2)	0.730(2)	0.031(1)	0.735(1)	0.121(6)
C(202)	0.280(3)	0.569(3)	−0.040(2)	0.058(13)	O(21)	0.704(2)	0.065(2)	0.801(2)	0.102(11)
C(203)	0.264(4)	0.493(3)	−0.092(2)	0.086(16)	O(22)	0.776(5)	−0.013(4)	0.743(3)	0.269(30)
C(204)	0.252(3)	0.421(2)	−0.073(2)	0.049(12)	O(23)	0.798(4)	0.100(3)	0.720(3)	0.216(22)
C(205)	0.260(3)	0.433(3)	0.001(2)	0.050(12)	O(24)	0.661(5)	0.010(4)	0.677(3)	0.247(27)
N(21)	0.272(2)	0.503(2)	0.053(2)	0.046(9)	Cl(3)	−0.259(1)	−0.125(1)	0.404(1)	0.118(6)
C(206)	0.238(3)	0.348(2)	0.024(2)	0.059(13)	O(25)	−0.308(4)	−0.082(3)	0.380(2)	0.186(20)
N(22)	0.286(2)	0.373(2)	0.106(2)	0.050(10)	O(26)	−0.248(5)	−0.182(4)	0.346(4)	0.294(31)
C(207)	0.381(3)	0.359(2)	0.119(2)	0.060(13)	O(27)	−0.281(5)	−0.136(4)	0.463(4)	0.313(35)
C(208)	0.482(3)	0.430(2)	0.119(2)	0.034(11)	O(28)	−0.153(4)	−0.081(3)	0.434(3)	0.192(19)
C(209)	0.518(3)	0.513(3)	0.187(2)	0.065(14)	Cl(4)	−0.380(2)	0.326(1)	0.244(1)	0.135(6)
N(23)	0.456(2)	0.562(2)	0.175(2)	0.046(9)	O(29)	−0.326(3)	0.313(2)	0.305(2)	0.129(14)
C(210)	0.497(3)	0.644(2)	0.244(2)	0.057(13)	O(30)	−0.408(4)	0.388(4)	0.275(3)	0.226(24)
C(211)	0.421(3)	0.681(3)	0.241(2)	0.048(12)	O(31)	−0.363(5)	0.318(4)	0.181(4)	0.279(30)
C(212)	0.445(3)	0.766(3)	0.274(2)	0.049(12)	O(32)	−0.484(7)	0.261(5)	0.218(4)	0.370(41)
C(213)	0.365(3)	0.788(3)	0.274(2)	0.059(13)	H2O(1)	0.041(3)	0.337(3)	−0.245(2)	0.179(18)
C(214)	0.260(3)	0.728(3)	0.243(2)	0.059(13)	H2O(2)	0.129(3)	0.490(3)	−0.257(2)	0.176(17)
C(215)	0.245(3)	0.646(3)	0.212(2)	0.049(12)	H2O(3)	0.001(6)	0.438(5)	−0.101(4)	0.366(38)
N(24)	0.315(3)	0.617(2)	0.209(2)	0.054(10)					

$^a U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \cdot a_i \cdot a_j$.

Table 3. {[MoO₄Crbispictn]₄}(ClO₄)₄·3H₂O selected interatomic distances (in Å) and angles (in °), t = terminal Mo–O, b = bridge O *trans* to t, c = O bonded to Cr, d = bridge O *trans* to c, n = number of chemically equivalent bonds or angles.

Atoms		Range	n	Mean[a]
Mo–Mo	short	3.188(5)–3.208(5)	2	3.198(10)
Mo–Mo	long	3.457(6)–3.490(6)	4	3.474(8)
Mo–O	t	1.58(3) –1.65(2)	4	1.622(15)
Mo–O	b	2.30(2) –2.42(2)	4	2.358(28)
Mo–O	c	1.79(2) –1.91(2)	8	1.827(16)
Mo–O	d	1.97(2) –2.07(2)	8	2.031(17)
Cr–O		1.84(2) –1.93(2)	8	1.888(13)
Cr–N		1.99(2) –2.09(2)	16	2.067(7)
O–Mo–O	dd, bd	70.8(8) – 76.9(9)	12	73.4(6)
O–Mo–O	ct	101.1(11)–104.9(11)	8	102.9(5)
O–Mo–O	cc	97.1(10)–100.1(9)	4	98.8(6)
O–Mo–O	tb	167.1(9) –171.2(10)	4	168.2(10)
O–Mo–O	cd	153.3(9) –157.1(10)	8	155.2(5)
O–Mo–O	td	95.0(10)– 98.3(10)	8	97.2(6)
O–Mo–O	bc	81.7(9) – 86.6(9)	8	84.5(5)
O–Mo–O	cd	86.1(9) – 95.1(9)	8	90.3(12)
Mo–O–Mo	dd, bd	102.7(9) –106.5(10)	12	104.4(6)
Mo–O–Cr		139.7(13)–142.9(13)	8	142.4(6)
O–Cr–O		88.5(9) – 93.0(10)	4	90.9(10)
O–Cr–N	cis	87.9(11)– 95.8(11)	24	91.8(4)
O–Cr–N	trans	170.4(11)–173.7(11)	8	172.0(4)
N–Cr–N	cis	76.9(13)–100.0(12)	20	87.8(15)
N–Cr–N	trans	171.9(12)–177.2(13)	4	174.7(11)

[a]Standard deviation of mean = $[\Sigma(x - \bar{x})^2]^{\frac{1}{2}} / n / (n-1)$.

4. {[WO₄Crbispictn]₄}(ClO₄)₄·10H₂O was prepared exactly as described for 1, but from [Crbispictn(OH)(H₂O)]-(ClO₄)₂·2H₂O (0.231 g, 0.40 mmol) and K₂WCl₆ (0.095 g, 0.20 mmol). Yield: 0.020 g of large, red crystals (14%). Anal. Calcd. for {[WO₄Cr(C₁₅H₂₀N₄)]₄}(ClO₄)₄·10H₂O: W 26.24, Cr 7.42, C 25.71, H 3.60, N 8.00, Cl 5.06. Found: W 26.74, Cr 7.53, C 25.71, H 3.26, N 7.95, Cl 5.05.

5. {[WO₄Crbispictn]₄}I₄·12H₂O was prepared as described for 1, but from [Crbispictn(OH)(H₂O)]I₂·2H₂O (0.253 g, 0.40 mmol) and K₂WCl₆ (0.095 g, 0.20 mmol). Yield: 0.066 g (45%). Anal. Calcd. for {[WO₄Crbispictn]₄}I₄·10H₂O: W 24.94, Cr 7.05, C 24.44, H 3.55, N 7.60, I 17.22. Found: W 24.42, Cr 7.00, C 24.81, H 3.16, N 7.61, I 16.45.

All the compounds described above had a tendency to crystallize with varying amounts of crystal water.

Crystal structure determination. Cell dimensions were determined from reflections measured at 4 positions: $2\theta, \omega, \chi, \varphi$; $-2\theta, -\omega, \chi, \varphi$; $2\theta, \omega, 180+\chi, \varphi$ and $-2\theta, -\omega, 180+\chi, \varphi$. Intensities were measured at room temperature using a Huber diffractometer and Nb-filtered MoKα radiation. The intensities of two standard reflections were measured every 50 reflections. Crystal data are given in Table 1.

Data were corrected for background, Lorentz and polarization effects and for absorption. Structures were determined using MULTAN80[9] and subsequent difference electron-density maps. The structures were refined by the least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$ using a modification of ORFLS.[10] W and Cr were refined with anisotropic thermal parameters, C, N and O with isotropic thermal parameters, and H atoms could not be located. Results are given in Tables 2 and 3.

Results and discussion

Synthetic aspects. In recent publications[6,11-13] we have demonstrated the capability of cations of the general formula cis-[M^III A₄(OH)₂]⁺ to act as chelate, bidentate ligands to bivalent and tervalent ions [M^III is chromium(III) or cobalt(III), and A₄ represents four ligating nitrogen atoms from ammonia, two bidentate or one tetradentate amine ligand]. In an identical procedure we tried to make a similar complex with molybdenum(III) as central atom and cis-β-[Crbispictn(OH)₂]⁺. The resulting product, however, was the abovementioned octanuclear complex with a cubane core of Mo^VI₄O₈^8+. An isomorphous compound was obtained from cis-β-[Cobispictn(OH)₂]⁺. The chromium complex could be synthesized from any soluble compound containing molybdenum in an oxidation state below six. In order to obtain the desired compound from sodium molybdate(VI) it was necessary to add a reducing agent. The corresponding octanuclear compound with a cubane core of W^VI₄O₈^8+ could be synthesized from potassium hexachlorotungstate(IV). All the compounds were soluble in water and N-methylformamide, and the solutions were stable.
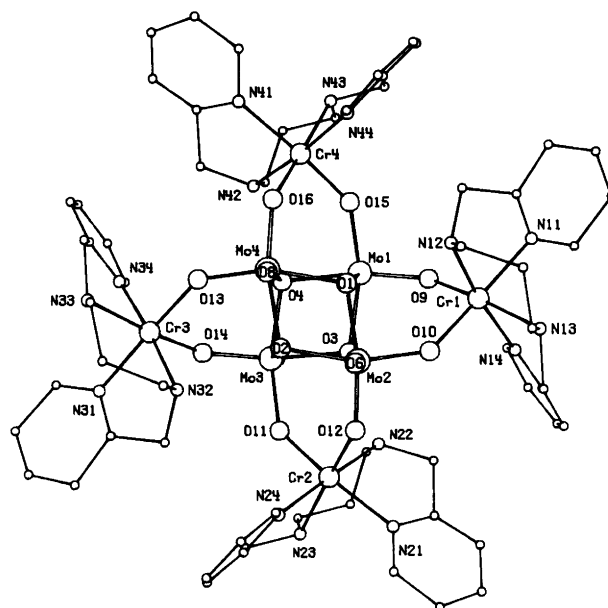

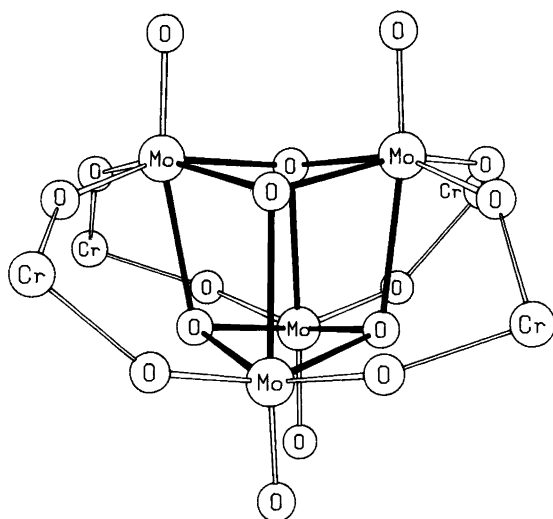Fig. 3. A perspective view of the cation. Atom O5 is hidden behind Mo1 and O7 is behind Mo3.

Fig. 4. A perspective view of the Mo_4O_4 cube.

Description of the structure. The cation (Fig. 3) has approximate $\overline{4}$ (S_4) symmetry. The complex is built up about a distorted cube of molybdenum and oxygen atoms (Fig. 4). There are four chemically distinct molybdenum–oxygen distances; the mean values for these are: $Mo-O_t$ = 1.622(15) Å, $Mo-O_b$ = 2.358(28) Å, $M-O_c$ = 1.827(16) Å and $M-O_d$ 2.031(16) Å (t = terminal, b = bridge oxygen *trans* to O_t, c = bonded to Cr, d = bridge oxygen *trans* to O_c). The internal O–Mo–O angles have a mean value of 73.4(6)° and the external ones 101.5(7)°; angles involving only one M–O within the cube are closer to right angles, O–Mo–O$_c$ = 87.4(10)° and O–Mo–O$_t$ = 97.2(6)°. Since repulsion between strong bonds is greater than that between weak ones, angles ct > cc and cd > bc. Angles at the oxygen atoms are Mo–O–Mo = 104.3(5)° and Mo–O–Cr = 142.4(6)°. There are two short Mo–Mo distances, 3.188(5) and 3.208(5) Å, and four long ones, 3.457(6)–3.490(6) Å. The short Mo–Mo distances are somewhat shorter than those found in $M_4(OH)_4$ (M = Mo or W) carbonyl and nitrosyl complexes,[14–17] i.e. 3.4–3.7 Å; however, the acute O–Mo–O angles show that, as expected for a full-shell configuration, there is no metal–metal bonding.[18]

The geometry at each chromium centre is approximately octahedral, with Cr–O = 1.888(13) Å and Cr–N = 2.067(7) Å. The ligands bind in the *cis*-β form, the configuration at the secondary nitrogen atoms [N(12),N(13),N(32),N(33)] is the same, being *S* in the enantiomer shown in Fig. 3, whereas at atoms [N(22),N(23),(N42),N(43)] it is *R*. The conformation at Cr(1) and Cr(3) is Δ and at Cr(2) and Cr(4) is Λ. Thus the complex ion shown in Fig. 3 is the $\Delta(\beta)(SS')\Lambda(\beta)(RR')\Delta(\beta)(SS')\Lambda(\beta)(RR')$ form.

Electronic spectra. The electronic spectra of the complexes with chromium (visible region) are shown in Fig. 5(a). The intensities of the first absorption bands ($\varepsilon/4$ = 165 at 512 nm in water, $\varepsilon/4$ = 164 at 518 nm in N-methylformamide)
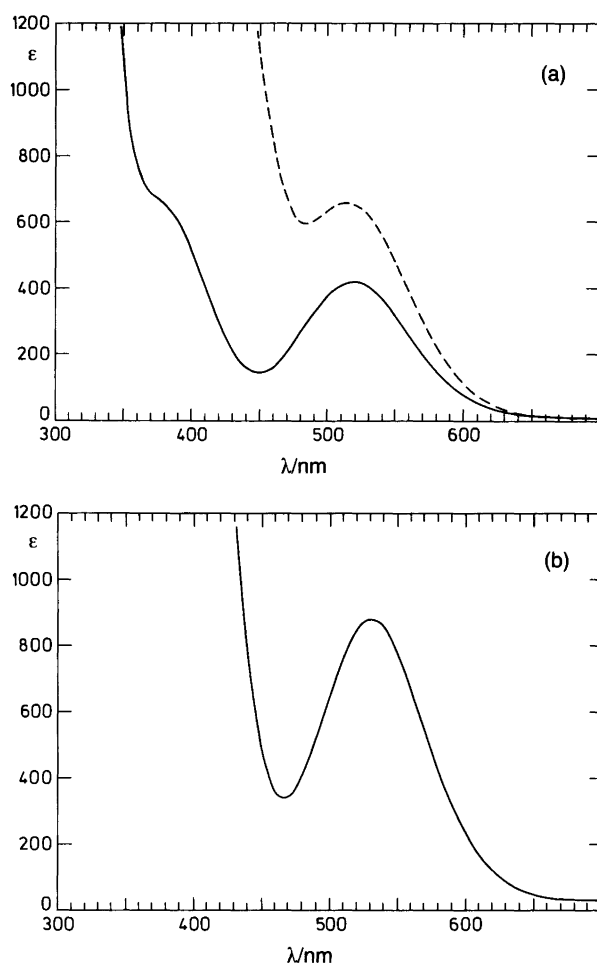

Fig. 5. (a) The absorption spectra (visible region) of $[MoO_4Crbispictn]_4^{4+}$ (— — — —) and $[Wo_4Crbispictn]_4^{4+}$ (———) in water. (b) The absorption spectrum (visible region) of $[MoO_4Cobispictn]_4^{4+}$ in water.

for the molybdenum compound and ($\varepsilon/4$ = 106 at 519 nm in water, $\varepsilon/4$ = 100 at 525 nm in N-methylformamide) for the tungsten compound are remarkably high, especially in the former case compared to the intensity of the first absorption band of the parentage mononuclear species *cis*-β-[Crbispictn(OH)(H$_2$O)]$^{2+}$ (ε = 74 at 513 nm in water). A similar high intensity is recognised in the case of the cobalt complex ($\varepsilon/4$ = 221 at 531 nm in water, $\varepsilon/4$ = 240 at 535 nm in N-methylformamide) compared to the corresponding value for [Cobispictn(OH)(H$_2$O)]$^{2+}$ (ε = 108 at 507 nm in water). The steep rise in intensity at ca. 450 nm in the molybdenum complexes may be a result of charge transfer from the oxygen p-orbitals to empty d-orbitals on the molybdenum (*vide infra*).

The magnetic susceptibility. The temperature dependence of the magnetic susceptibility of {[MoO$_4$Cr(bispictn)]$_4$}-(ClO$_4$)$_4$·10H$_2$O, was measured in the temperature range 4–300 K as shown in Fig. 6. The susceptibility shows a maximum at ca. 45 K and the effective magnetic moment
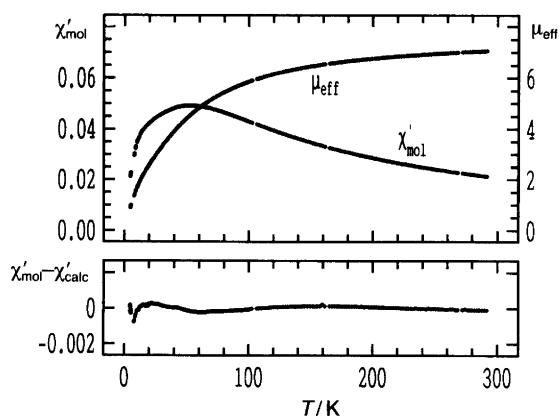
Fig. 6. The magnetic susceptibility (in c.g.s. units) and the effective magnetic moment as a function of temperature for {[MoO₄Crbispictn]₄}(ClO₄)₄·10H₂O.The lower graph gives the difference between the measured and calculated susceptibilities.
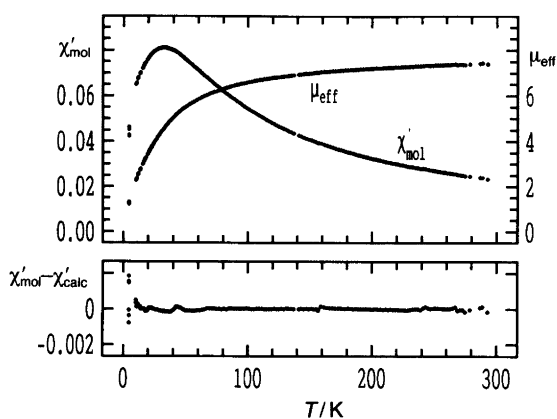

Fig. 7. The magnetic susceptibility (in c.g.s. units) and the effective magnetic moment as a function of temperature for {[WO₄Crbispictn]₄}(ClO₄)₄·4H₂O. The lower graph gives the difference between the measured and calculated susceptibilities.

declines from 7.1 μ_B at room temperature to 2 μ_B at 4 K. The susceptibility data for the complex {[WO₄Cr(bis-pictn)]₄}(ClO₄)₄·4H₂O in Fig. 7 shows similar behaviour, with a susceptibility maximum at 30 K and a magnetic moment at room temperature of 7.3 μ_B. This is the expected behaviour characteristic for weakly antiferromagnetically coupled tetranuclear chromium(III) complexes. For an uncoupled tetranuclear chromium(III) complex with g values of 2 the expected magnetic moment is 7.75 μ_B.

The temperature dependence of the magnetic susceptibilities $\chi'_{mol,exp}$ were approximated by eqn. (1), by

$$\chi'_{mol,exp} \approx \chi'_{mol,calc} = -\frac{N}{H}\frac{\sum_i \frac{\partial E_i}{\partial H} \exp\left(-E_i/kT\right)}{\sum_i \exp\left(-E_i/kT\right)} + K + C/T \quad (1)$$

minimization of eqn. (2) within the framework of nonlinear

$$\sum_i \frac{[\chi'_{mol,exp}(T) - \chi'_{mol,calc}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial \chi}{\partial T}\right)^2 \sigma^2(T)} \quad (2)$$

regression analysis. $\sigma(\chi')$ and $\sigma(T)$ are the estimated standard deviations on the measured magnetic susceptibility and temperature, respectively. In eqn. (1) C/T accounts for paramagnetic impurities, while K accounts for temperature-independent paramagnetism and minor deviations in the correction for diamagnetism. The energies E_i of the 256 components of the ground-state manifold were obtained by means of the isotropic spin Hamilton operator eqn. (3),

$$\hat{H} = \sum_{i=1}^{4} g\mu_B \hat{S}_i \cdot \hat{H} + J\sum_{i=1}^{4} \hat{S}_i \cdot \hat{S}_{(i+1)mod4} + J'\sum_{i=1}^{2} \hat{S}_i \cdot \hat{S}_{i+2} \quad (3)$$

where we have assumed that the g values for the four chromium atoms are identical. The second term in eqn. (3) accounts for interactions between neighbouring chromium atoms, and the last term accounts for the interaction between opposite chromium atoms.

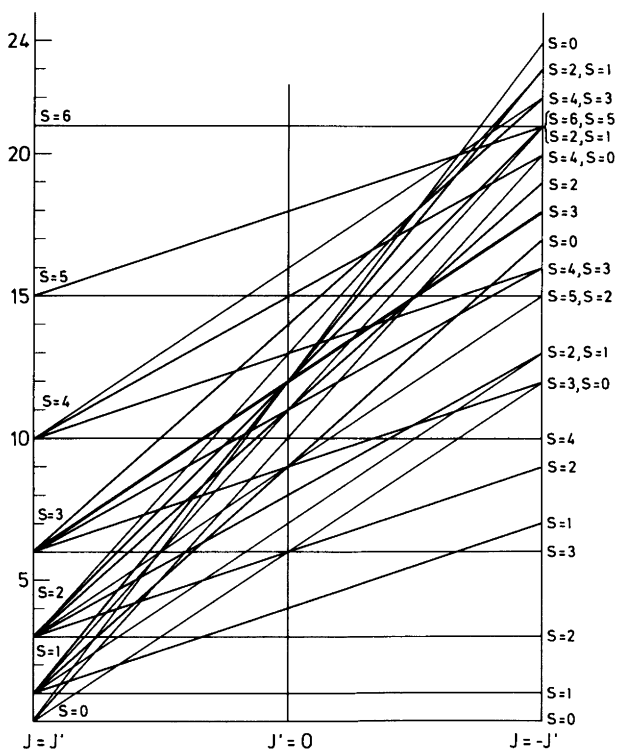The relative energies of the different spin states are shown in Fig. 8, where the x-axis describes the relative size

Fig. 8. The relative energies of the different spin states from eqn. (3) in units of J. To the left J = J', which represents the situation where the interaction between the four chromium atoms are equivalent. To the right J = −J'. The thickness of the lines gives their degeneracies. The thickest lines are triply degenerate and the middle lines doubly degenerate, while the thinnest are non-degenerate.

Table 4. Values given by the minimization (see text).

Compound	J	J'	g	Var/f
{[MoO$_4$Cr(bispictn)]$_4$}(ClO$_4$)$_4$·10H$_2$O	14.60	−1.18	1.982	8.7
{[MoO$_4$Cr(bispictn)]$_4$}I$_4$·12H$_2$O	14.44	−2.74	1.942	13.2
{[WO$_4$Cr(bispictn)]$_4$}(ClO$_4$)$_4$·4H$_2$O	9.66	1.01	1.990	1.15
{[WO$_4$Cr(bispictn)]$_4$}I$_4$·6H$_2$O	9.41	1.03	1.987	1.90

of J and J'. It is seen that the ground state is always a singlet and that other singlets lie a little higher in energy before a triplet state appears. Furthermore, the diagram is rather complicated, with many states with different spin values close together, which might explain why no EPR spectra are observed in the temperature range 4–300 K, except for some broad and uncharacteristic signals.

The parameters obtained by the minimization are given in Table 4. It is seen that the interactions between neighbouring chromium atoms are more important than the interactions between opposite chromium atoms. The J values are relative high, considering that the π-interactions in the complexes have to extend through four bonds.[18,19] The negative sign for J', i.e. a ferromagnetic interaction between opposite chromium atoms in the molybdenum complexes, is not understood at present; however, interactions between opposite chromium atoms have to extend through six or eight bonds, whereby they become small.

To understand the antiferromagnetic interaction between neighbouring chromium atoms the interaction is expanded[19] on the orbitals of the intervening atoms. In this way J becomes proportional to the square of the overlap integral between the p-orbitals on oxygen and the empty d-orbitals on Mo or W, and is furthermore multiplied by the overlap integral between linear combinations of d-orbitals which have maximum overlap with the p-orbitals on the two oxygen atoms. Since the two sets of d-orbitals on Mo or W are not orthogonal, the antiferromagnetic contribution does not vanish. This gives eqn. (4) for the interaction

$$J = \frac{\left(\frac{4}{\sqrt{3}}e_{\pi 0}\right)^2}{E_{ct}}\left[\langle p_0|\frac{1}{\sqrt{2}}(\eta-\xi)\rangle\langle\frac{1}{\sqrt{2}}(\eta-\xi)|\frac{1}{\sqrt{2}}(\xi-\zeta)\rangle\right.$$
$$\left.\langle\frac{1}{\sqrt{2}}(\xi-\zeta)|p_0\rangle\right]^2$$

$$=\frac{1}{4}\frac{\left(\frac{4}{\sqrt{3}}e_{\pi 0}\right)^2}{E_{ct}}\left[\langle p_0|\frac{1}{\sqrt{2}}(\eta-\xi)\rangle\langle\frac{1}{\sqrt{2}}(\xi-\zeta)|p_0\rangle\right]^2 \quad (4)$$

between Cr1 and Cr2 via the p-orbitals on O10 and O12 and the linear combinations of d-orbitals on the Mo2, which have maximum overlap with the oxygen p-orbitals.

The overlap integrals in the last part of eqn. (4) must be greater in the case of molybdenum than in the case of tungsten, because molybdenum(VI) is easier to reduce than tungsten(VI). This charge transfer is also seen in the UV–VIS spectra, where charge transfer to the empty d-orbitals is at a much lower energy in the molybdenum complexes than in the tungsten complexes. This explains why J is bigger for the molybdenum complexes than for the tungsten complexes.

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