Acta Chemica Scandinavica, 1996: 50: 95–101
Printed in Belgium – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Crystal Structures of Dinuclear Copper(II) and Oxovanadium(IV) Complexes of *N,N,N′,N′*-Tetrakis(2-pyridylmethyl)-6,6′-bis(aminomethyl)-2,2′-bipyridine

Anders Døssing,[†,a] Alan Hazell[b] and Hans Toftlund[c]

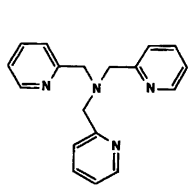
[a]Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark, [b]Department of Chemistry, Aarhus University, DK-8000 Århus C, Denmark and [c]Department of Chemistry, Odense University, DK-5540 Odense M, Denmark

Døssing, A., Hazell, A. and Toftlund, H., 1996. Crystal Structures of Dinuclear Copper(II) and Oxovanadium(IV) Complexes of *N,N,N′,N′*-Tetrakis(2-pyridylmethyl)-6,6′-bis(aminomethyl)-2,2′-bipyridine. – Acta Chem. Scand. 50: 95–101 © Acta Chemica Scandinavica 1996.

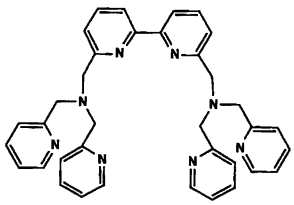
Two dinuclear transition-metal complexes of the polypyridine ligand *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-6,6′-bis(aminomethyl)-2,2′-bipyridine (btpa) have been prepared and structurally characterized. The crystal structure of $[Cu_2(SO_4)_2(btpa)]_{0.68(1)}[Cu_2(SO_4)_2(H_2O)_2(btpa]_{0.32(1)}\cdot 6.64(2)H_2O$ (**1**) is triclinic, space group $P\bar{1}$, with $a = 9.197(3)$, $b = 8.357(2)$, $c = 14.490(5)$ Å, $\alpha = 103.98(2)$, $\beta = 90.95(2)$, $\gamma = 93.41(1)°$ with one formula unit in the cell. The structure refined to a final *R*-value of 0.058 for 1686 reflexions. There is a square-planar arrangement of an oxygen atom of the sulfate ion and three nitrogen atoms of the btpa ligand which bridges the two copper atoms of the centrosymmetric complex cation, Cu···Cu = 7.718(4) Å. The structure is disordered with a water molecule sometimes coordinating to the copper atom. The crystal structure of $[(VO)_2(\mu\text{-}SO_4)(btpa)](ClO_4)_2\cdot 4.99(8)H_2O$ (**2**) is triclinic, space group $P\bar{1}$, with $a = 16.710(3)$, $b = 10.813(2)$, $c = 13.845(2)$ Å, $\alpha = 100.76(1)$, $\beta = 95.42(1)$, $\gamma = 102.89(1)°$ with two formula units in the cell. The structure refined to a final *R*-value of 0.064 for 4120 reflexions. The vanadyl groups of the complex dimer are bridged by btpa and by a sulfate ion, V···V = 4.328(2) Å. The vanadium atoms are octahedrally coordinated by a vanadyl oxygen atom, an oxygen of the sulfate ion and four nitrogen atoms of btpa. Magnetic measurements show no magnetic interaction between the metal centers in **1** or in **2**.

In recent years we[1,2] and others[3–5] have studied magnetic, spectral and other properties of dinuclear transition-metal complexes of the tetradentate, tripodal ligand tris(2-pyridylmethyl)amine (tpa) where the two metal centers are bridged by various ligands. In particular, copper(II) complexes of tpa containing a peroxo bridge have attracted considerable attention lately because of interest in mimicking the active centers in the copper proteins hemocyanin and tyrosinase.[6] The rich chemistry of the dinuclear metal–tpa complexes has in this context prompted us to focus our attention on the preparation and characterization of dinuclear metal complexes of the polypyridine ligand *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-6,6′-bis(aminomethyl)-2,2′-bipyridine (btpa).

The btpa ligand is interesting because it may be regarded as a dimeric form of tpa and thereby capable of binding two metal ions. The ligand was first prepared on small scale by Dürr,[7] but no metal complexes have to the best of our knowledge been reported. The synthesis and structural characterization of a dinuclear copper(II) and a dinuclear oxovanadium(IV) complex of btpa is reported here.



tpa



btpa

Experimental

Materials. The compound 6,6′-bis(bromomethyl)-2,2′-bipyridine[8] was prepared by a literature procedure. Bis(2-pyridylmethyl)amine was purchased from Nepera and

† To whom correspondence should be addressed.

distilled prior to use. The preparation of the ligand btpa is a modification of the method of Dürr.[7] All other chemicals were reagent grade and were used without further purification.

N,N,N′,N′-tetrakis(2-pyridylmethyl)-6,6′-bis(aminomethyl)-2,2′-bipyridine (btpa). Bis(2-pyridylmethyl)amine (6.00 g, 30.1 mmol) was dissolved in acetonitrile (800 ml), and Na_2CO_3 (30 g) were added. The mixture was refluxed and stirred and 6,6′-bis(bromomethyl)-2,2′-bipyridine (5.15 g, 15.1 mmol) was added in small portions within 3 h. The mixture was refluxed overnight, then cooled to room temperature and filtered. The filtrate was evaporated to a dark-brown oil which was redissolved in ethanol (400 ml) and added dropwise to a solution of $CuSO_4 \cdot 5H_2O$ (8.3 g, 33 mmol) in H_2O (600 ml). The blue precipitate of $[Cu_2(SO_4)_2(btpa)] \cdot aq$ was filtered off and washed with an ethanol–water mixture (1:1), ethanol and diethyl ether and air-dried (10.4 g). For decomplexation the complex was added to a solution of 12 M NH_3 (400 ml). CH_2Cl_2 (300 ml) was then added and the mixture was stirred vigorously until the aqueous phase was clear and blue. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 300 ml). The combined organic solutions were dried (Na_2SO_4) and the solvent was removed, leaving white btpa (5.8 g, 67%). If the product at this stage was colored the complexation–decomplexation cycle was repeated. Anal. Calc. for $C_{36}H_{34}N_8$: C, 74.72; H, 5.92; N, 19.36. Found: C, 74.59; H, 5.91; N, 19.36. m.p. 155°C. UV–vis (CH_3OH, λ_{max}/nm, $\varepsilon_{max}/M^{-1}\ cm^{-1}$): (288, 17.2×10^3), (267, 19.4×10^3), (261, 20.3×10^3) and (246, 15.3×10^3) The ^1H NMR spectrum was identical to that reported by Dürr.[7]

$[Cu_2(SO_4)_2(btpa)]_{0.68(1)}[Cu_2(SO_4)_2(H_2O)_2(btpa)]_{0.32(1)} \cdot 6.64(2)H_2O$ (**1**). $CuSO_4 \cdot 5H_2O$ (78 mg, 0.312 mmol) was dissolved in H_2O (10 ml). Then a solution of btpa (89 mg, 0.154 mmol) in ethanol was added. The resultant blue solution was left for slow evaporation yielding large, blue crystals. These were washed with ethanol, diethyl ether and air-dried. Yield 141 mg, (89%). Anal. Calc. for $C_{36}H_{48.56}N_8Cu_2O_{15.28}S_2$: C, 42.02; H, 4.76; N, 10.89; Cu,

Table 1. Crystallographic data for compounds **1** and **2**.

	1	**2**
Chemical formula	$Cu_2S_2O_{15.28}N_8C_{36}H_{48.56}$	$V_2Cl_2SO_{18.99}N_8C_{36}H_{43.98}$
FW/g mol^{-1}	1029.04	1097.47
Space group	$P\bar{1}$	$P\bar{1}$
Cell parameters (249 K)		
a/Å	9.197(3)	16.710(3)
b/Å	8.357(2)	10.813(2)
c/Å	14.490(5)	13.845(2)
α/°	103.98(2)	100.76(1)
β/°	90.95(2)	95.42(1)
γ/°	93.41(1)	102.89(1)
V/Å^3	1078.3(6)	2371.3(7)
No. of reflections centred	120	100
2θ range/°	15.0–23.3	20.0–20.7
Calculated density (294 K)/g cm^{-3}	1.585	1.538
Formula units per cell	1	2
Crystal size/mm^3	0.093×0.183×0.522	0.486×0.144×0.500
Development forms	{100}{010}{001}	{100}{010}{001}
Radiation (Mo Kα), λ/Å	0.71073	0.71073
Monochromator	Graphite	Graphite
Linear absorption coefficient, μ/cm^{-1}	11.56	6.15
Range of transmission factors	0.787–0.903	0.763–0.918
Scan type	ω–2θ	ω–2θ
ω-Scan width, Δθ/°	1.2+0.346 tan θ	1.2+0.346 tan θ
No. of steps	50	50
Time per step/s	1	1
θ-limits/°	1.5–27.5	1.5–25.0
Octants collected	$+h \pm k \pm l$	$+h \pm k \pm l$
Standard reflections	300,003	400,015
Fall-off in intensity (%)	4	5
No. of unique data	3979	8333
No. of data with $I/\sigma(I) > 3.0$	1686	4120
No. of variables	335	633
Weights, $w^{-1} = [\sigma_{CS}(F^2) + 1.03\ F^2]^{1/2} - \lvert F \rvert]$		
$R = \Sigma(\lvert F_o \rvert - \lvert F_c \rvert)/\Sigma \lvert F_o \rvert$	0.058	0.064
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/\Sigma w \lvert F_o \rvert^2]^{1/2}$	0.065	0.076
S	1.35	1.75
Δ/σ_{max}	0.87	0.13
$\Delta\rho_{max}$/e Å^{-3}	0.54(9)	0.71(8)

12.35. Found: C, 41.51; H, 4.43; N, 10.65; Cu, 12.46.UV–vis (H_2O, λ_{max}/nm, $\varepsilon_{max}/M^{-1}\ cm^{-1}$): (829, 167), (691, 170), (285, 10.9×10^3) and (257, 22.7×10^3).

[(VO)$_2$(μ-SO$_4$)(btpa)][ClO$_4$)$_2$·H$_2$O (**2**). $VOSO_4 \cdot 5H_2O$ (66 mg, 0.33 mmol) and btpa (75 mg, 0.13 mmol) were stirred in water (4 ml) until a clear blue–violet solution was obtained. Then CH_3CN (4 ml) and $LiClO_4$ (90 mg) were added, and the solution was filtered and left overnight for slow evaporation yielding a blue–violet product. This was washed successively with 2 M $LiClO_4$, ethanol and diethyl ether and finally air-dried. (108 mg, 81%). Anal. Calc. for $C_{36}H_{36}N_8Cl_2O_{15}SV_2$: C, 42.16; H, 3.54; N, 10.93; Cl, 6.91. Found: C, 42.05; H, 3.54; N, 11.13; Cl, 6.92. UV–vis (CH_3CN, λ_{max}/nm, $\varepsilon_{max}/M^{-1}\ cm^{-1}$): (742, 145), (566, 174), (366, 1.83×10^3) and (260, 22.8×10^3). IR (KBr): 981 cm^{-1} (V = O). Crystals for X-ray crystallography were made by slow evaporation of an aqueous solution of **2**. The content of crystal water in these crystals is higher than in the previous product.

X-Ray crystallography. Single crystals of **1** and **2** were mounted on a Huber four-circle diffractometer. Cell dimensions were determined from reflexions measured at $\pm 2\theta$ and high and low χ. Intensities were measured at room temperature, two standard reflexions were monitored every 50 reflexions. Crystal data are given in Table 1. Data were corrected for background, Lorentz and polarization effects, decay and for absorption. The structures were determined using SIR92[9] and from subsequent difference electron density maps and were refined by the least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$ using a modification of ORLFS.[10] Unless otherwise stated, hydrogen atom positions on the ligands were kept at calculated positions with C–H = 0.95 Å and U_{iso} 20% larger than U_{eq} for the atom to which it was attached. Uncoordinated water molecules were considered to be free rotors. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Table 2. $[Cu_2(SO_4)_2(btpa)]_{0.68(1)}[Cu_2(SO_4)_2(H_2O)_2(btpa)]_{0.32(1)} \cdot 6.64(2) \cdot H_2O$ fractional coordinates, equivalent isotropic thermal parameters (in Å^2) and occupation factors (where not unity).

Atom	*x*	*y*	*z*	U_{eq} [a]	occ
Cu	0.01605(16)	−0.06284(19)	0.22770(10)	0.047	
S	−0.2679(7)	−0.0501(8)	0.1426(5)	0.040	0.68(1)
O(1)	−0.1949(7)	−0.0796(9)	0.2320(5)	0.049	
O(2)	−0.3534(17)	−0.2041(19)	0.0929(11)	0.069	0.68
O(3)	−0.3639(15)	0.0848(15)	0.1674(10)	0.067	0.68
O(4)	−0.1487(13)	−0.0133(15)	0.0857(7)	0.064	0.68
N(1)	0.2338(10)	−0.0494(12)	0.2121(6)	0.054	
C(11)	0.2560(14)	−0.1714(18)	0.1218(8)	0.073	
C(12)	0.1629(14)	−0.3251(16)	0.1193(7)	0.061	
C(13)	0.1932(19)	−0.4844(20)	0.0722(9)	0.093	
C(14)	0.1001(23)	−0.6110(19)	0.0715(10)	0.095	
C(15)	−0.0326(18)	−0.5890(15)	0.1193(9)	0.080	
C(16)	−0.0579(15)	−0.4213(15)	0.1655(7)	0.059	
N(17)	0.0340(11)	−0.3001(11)	0.1657(6)	0.050	
C(21)	0.2768(12)	0.1251(17)	0.2083(8)	0.064	
C(22)	0.1783(13)	0.2427(17)	0.2716(8)	0.053	
C(23)	0.2226(14)	0.4078(19)	0.3124(10)	0.073	
C(24)	0.1217(19)	0.5024(16)	0.3649(10)	0.078	
C(25)	−0.0129(17)	0.4377(17)	0.3765(9)	0.065	
C(26)	−0.0492(12)	0.2750(16)	0.3354(8)	0.055	
N(27)	0.0485(9)	0.1779(9)	0.2823(6)	0.037	
C(31)	0.3159(11)	−0.0956(15)	0.2905(8)	0.055	
C(32)	0.2639(11)	−0.0122(13)	0.3877(7)	0.042	
C(33)	0.3570(11)	0.0974(16)	0.4514(9)	0.058	
C(34)	0.3070(13)	0.1727(18)	0.5403(9)	0.073	
C(35)	0.1657(14)	0.1333(16)	0.5589(8)	0.060	
C(36)	0.0772(10)	0.0228(13)	0.4922(7)	0.042	
N(37)	0.1284(9)	−0.0479(10)	0.4059(6)	0.040	
O(5)	−0.5152(11)	−0.2805(10)	−0.0669(6)	0.097	
O(6)	0.5425(11)	−0.4257(11)	0.2058(7)	0.108	
O(7)	−0.3867(12)	0.3865(18)	0.3289(11)	0.177	
S′	−0.3070(16)	−0.0141(20)	0.1875(14)	0.050	0.32
O(2′)	−0.3837(22)	0.0917(32)	0.2634(20)	0.068	0.32
O(3′)	−0.2606(28)	0.0820(28)	0.1233(21)	0.060	0.32
O(4′)	−0.3953(46)	−0.1523(32)	0.1388(23)	0.063	0.32
O(5′)	0.0093(26)	0.0120(29)	0.0719(15)	0.056	0.32
O(6′)	−0.4026(32)	0.3986(39)	−0.4961(21)	0.104	0.32

[a] $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

$[Cu_2(SO_4)_2(btpa)]_{0.68(1)}[Cu_2(SO_4)_2(H_2O)_2(btpa)]_{0.32(1)}\cdot 6.64(2)H_2O$ (**1**). The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with one formula unit in the cell. Data were collected in the range $3 < 2\theta < 55°$. The structure was found to be disordered, S, O(2), O(3) and O(4) were constrained to have the same occupation factor, occ = 0.68(1), and S′, O(2′), O(3′), O(4′), O(5′) and O(6′) to have an occupation factor of 1 − occ. Fractional atomic coordinates are listed in Table 2, selected bond distances and angles in Table 3.

$[(VO)_2(\mu\text{-}SO_4)(btpa)](ClO_4)_2\cdot 4.99(8)H_2O$ (**2**). The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with two formula units in the cell. Data were collected in the range $3 < 2\theta < 50°$. The water molecules were disordered and the molecules were refined with individual occupation factors giving 4.99(8) in the asymmetric unit. Fractional atomic coordinates are listed in Table 4, selected bond distances and angles in Table 5. The atomic scattering factors were from Ref. 11, as were the anomalous scattering corrections for Cu and V. Thermal parameters, structure factors and hydrogen coordinates are available from the authors.

Other physical measurements. NMR spectra were recorded on a Bruker 250 MHz spectrometer, IR spectra were recorded on a on a Hitachi 270-30 infrared spectrophotometer, and optical absorption spectra were measured on a Perkin-Elmer Lamda 17 spectrophotometer. Magnetic susceptibilities were measured (at the University of Copenhagen) by the Faraday method on equipment described earlier.[12,13] The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants. The synthesized compounds were analyzed on a microscale in the Analytical Laboratory, University of Copenhagen.

Table 3. Selected distances (in Å), angles (in °) and torsion angles (in °) for compound **1**.[a]

Cu–Cu^{i}	7.718(4)	Cu–Cu^{ii}	6.932(4)
Cu–O(1)	1.940(7)	Cu–N(1)	2.018(9)
Cu–N(17)	1.987(9)	Cu–N(27)	1.979(8)
Cu–N(37)	2.737(8)	Cu–O(5′)	2.484(21)
Cu–O(4)	2.662(11)	S–S′	0.755(15)
O(1)–Cu–N(1)	175.6(3)	N(1)–Cu–O(5′)	83.7(6)
O(1)–Cu–N(17)	95.3(4)	N(17)–Cu–N(27)	166.1(4)
O(1)–Cu–N(27)	98.3(3)	N(17)–Cu–N(37)	100.7(3)
O(1)–Cu–N(37)	108.4(3)	N(17)–Cu–O(4)	93.4(4)
O(1)–Cu–O(5′)	92.3(6)	N(17)–Cu–O(5′)	92.0(6)
O(1)–Cu–O(4)	59.1(3)	N(27)–Cu–N(37)	77.5(3)
N(1)–Cu–N(17)	83.0(4)	N(27)–Cu–O(4)	91.3(3)
N(1)–Cu–N(27)	83.3(4)	N(27)–Cu–O(5′)	84.9(6)
N(1)–Cu–N(37)	76.0(3)	N(37)–Cu–O(4)	162.2(3)
N(1)–Cu–O(4)	116.8(4)	N(37)–Cu–O(5′)	154.4(6)
N(37)–C(36)–C(36^{i})–N(37^{i})	180.0		

[a] Symmetry ^{i} $-x, -y, 1-z$; ^{ii} $-x, -y, -z$.

Table 4. $[(VO)_2(\mu\text{-}SO_4)(btpa)](ClO_4)_2\cdot 4.99(8)H_2O$ fractional coordinates, equivalent isotropic thermal parameters (in Å^2) and occupation factors (where not unity).

Atom	*x*	y	*z*	U_{eq}[a]	occ
V(1)	0.30239(8)	0.22824(12)	−0.00209(9)	0.045	
V(2)	0.27105(8)	0.33173(11)	0.30699(9)	0.041	
S(1)	0.4253(1)	0.2908(2)	0.1999(1)	0.043	
O(1)	0.3102(3)	0.3800(5)	0.0196(4)	0.058	
O(2)	0.2438(3)	0.1778(4)	0.2731(3)	0.046	
O(3)	0.3652(3)	0.1974(4)	0.1151(3)	0.047	
O(4)	0.3771(3)	0.3792(4)	0.2522(3)	0.046	
O(5)	0.4911(3)	0.3701(5)	0.1624(4)	0.065	
O(6)	0.4523(4)	0.2155(5)	0.2654(4)	0.066	
N(1)	0.2881(4)	0.0132(6)	−0.0627(4)	0.052	
N(2)	0.2962(4)	0.5469(5)	0.3757(4)	0.047	
N(17)	0.2307(4)	0.1944(7)	−0.1434(4)	0.061	
N(27)	0.4076(4)	0.2235(6)	−0.0726(4)	0.047	
N(37)	0.1940(4)	0.1368(6)	0.0539(4)	0.046	
N(47)	0.1689(4)	0.3422(6)	0.3855(4)	0.043	
N(57)	0.3381(4)	0.3506(6)	0.4475(4)	0.047	
N(67)	0.2146(4)	0.4095(6)	0.1939(4)	0.045	
C(11)	0.2394(7)	−0.0282(9)	−0.1637(6)	0.084	
C(12)	0.2095(6)	0.0728(9)	−0.1999(6)	0.065	
C(13)	0.1644(8)	0.0451(12)	−0.2927(8)	0.116	
C(14)	0.1385(12)	0.1376(16)	−0.3279(9)	0.174	
C(15)	0.1611(11)	0.2652(15)	−0.2704(9)	0.168	
C(16)	0.2063(8)	0.2907(10)	−0.1778(7)	0.092	
C(21)	0.3735(6)	−0.0026(8)	−0.0671(6)	0.065	
C(22)	0.4288(5)	0.1102(8)	−0.0954(6)	0.053	
C(23)	0.4975(7)	0.1008(9)	−0.1413(7)	0.076	
C(24)	0.5491(7)	0.2105(11)	−0.1557(7)	0.082	
C(25)	0.5289(6)	0.3264(9)	−0.1291(7)	0.072	
C(26)	0.4576(6)	0.3289(8)	−0.0903(6)	0.058	
C(31)	0.2468(5)	−0.0537(7)	0.0084(6)	0.056	
C(32)	0.1804(5)	0.0066(8)	0.0458(5)	0.051	
C(33)	0.1123(6)	−0.0640(8)	0.0762(6)	0.064	
C(34)	0.0552(6)	−0.0038(10)	0.1162(7)	0.074	
C(35)	0.0694(6)	0.1294(9)	0.1280(6)	0.065	
C(36)	0.1394(5)	0.1970(8)	0.0974(5)	0.049	
C(41)	0.2266(6)	0.5746(8)	0.4278(6)	0.065	
C(42)	0.1657(5)	0.4546(7)	0.4404(5)	0.046	
C(43)	0.1082(6)	0.4641(9)	0.5049(6)	0.062	
C(44)	0.0509(6)	0.3555(10)	0.5104(6)	0.064	
C(45)	0.0526(6)	0.2381(9)	0.4516(7)	0.065	
C(46)	0.1117(5)	0.2333(8)	0.3911(6)	0.053	
C(51)	0.3744(5)	0.5775(8)	0.4436(5)	0.056	
C(52)	0.3760(5)	0.4733(8)	0.4993(5)	0.052	
C(53)	0.4136(6)	0.4954(10)	0.5959(6)	0.073	
C(54)	0.4148(7)	0.3926(12)	0.6384(7)	0.087	
C(55)	0.3775(6)	0.2678(9)	0.5859(7)	0.077	
C(56)	0.3410(5)	0.2521(8)	0.4899(6)	0.058	
C(61)	0.3022(5)	0.6114(7)	0.2915(6)	0.053	
C(62)	0.2352(5)	0.5399(8)	0.2063(5)	0.053	
C(63)	0.2001(6)	0.6046(9)	0.1443(7)	0.073	
C(64)	0.1420(7)	0.5339(11)	0.0647(7)	0.083	
C(65)	0.1201(6)	0.3993(9)	0.0490(6)	0.069	
C(66)	0.1580(5)	0.3421(7)	0.1137(6)	0.050	
Cl(1)	0.1464(2)	−0.1172(3)	0.4084(2)	0.086	
O(7)	0.0814(8)	−0.0633(11)	0.4100(12)	0.229	
O(8)	0.1382(7)	−0.1963(10)	0.4768(11)	0.209	
O(9)	0.1545(11)	−0.1808(20)	0.3251(9)	0.328	
O(10)	0.2139(9)	−0.0269(17)	0.4441(10)	0.283	
Cl(2)	−0.0757(3)	0.3784(3)	0.2127(2)	0.099	
O(11)	−0.0779(5)	0.3006(9)	0.1233(6)	0.137	
O(12)	−0.1222(14)	0.4535(18)	0.2070(12)	0.321	
O(13)	0.0056(10)	0.4423(15)	0.2544(9)	0.275	
O(14)	−0.1018(9)	0.3041(12)	0.2798(8)	0.223	
O(15)	−0.3374(5)	0.0361(7)	−0.2646(6)	0.111	0.93(2)
O(16)	−0.0097(7)	0.2923(11)	−0.1679(8)	0.113	0.65(2)
O(17)	0.6542(10)	0.3373(15)	0.1215(14)	0.256	0.83(3)
O(18)	0.5683(18)	0.0830(17)	0.5529(21)	0.416	0.76(4)
O(19)	0.6615(16)	0.0815(22)	0.3881(16)	0.323	0.77(4)
O(20)	0.7020(23)	0.3069(30)	0.2948(18)	0.384	0.72(4)
O(21)	0.6098(19)	0.1796(30)	0.3162(22)	0.136	0.33(3)

[a] $U_{eq} = 1/3\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 5. Selected distances (in Å), angles (in °) and torsion angles (in °) for compound **2**.

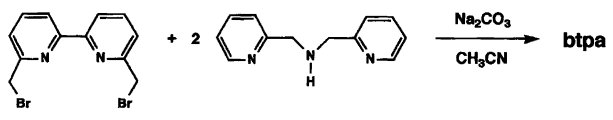
V(1)–O(1)	1.586(5)	V(2)–O(2)	1.590(5)
V(1)–O(3)	1.970(5)	V(2)–O(4)	1.993(5)
V(1)–N(1)	2.270(6)	V(2)–N(2)	2.271(6)
V(1)–N(17)	2.119(6)	V(2)–N(47)	2.121(6)
V(1)–N(27)	2.096(6)	V(2)–N(57)	2.102(6)
V(1)–N(37)	2.147(7)	V(2)–N(67)	2.147(6)
S(1)–O(3)	1.513(5)	S(1)–O(5)	1.438(6)
S(1)–O(4)	1.512(5)	S(1)–O(6)	1.432(6)
V(1)–V(2)	4.328(2)		
O(1)–V(1)–O(3)	105.3(2)	O(2)–V(2)–O(4)	103.5(2)
O(1)–V(1)–N(1)	169.5(3)	O(2)–V(2)–N(2)	170.3(2)
O(1)–V(1)–N(17)	93.7(3)	O(2)–V(2)–N(47)	93.8(2)
O(1)–V(1)–N(27)	99.1(3)	O(2)–V(2)–N(57)	99.8(2)
O(1)–V(1)–N(37)	108.4(3)	O(2)–V(2)–N(67)	107.4(2)
O(3)–V(1)–N(1)	84.1(3)	O(4)–V(2)–N(2)	85.5(2)
O(3)–V(1)–N(17)	161.0(2)	O(4)–V(2)–N(47)	162.6(2)
O(3)–V(1)–N(27)	87.2(2)	O(4)–V(2)–N(57)	90.0(2)
O(3)–V(1)–N(37)	85.5(2)	O(4)–V(2)–N(67)	87.5(2)
N(1)–V(1)–N(17)	76.9(2)	N(2)–V(2)–N(47)	77.1(2)
N(1)–V(1)–N(27)	76.5(2)	N(2)–V(2)–N(57)	76.2(2)
N(1)–V(1)–N(37)	76.4(3)	N(2)–V(2)–N(67)	76.2(2)
N(17)–V(1)–N(27)	89.0(2)	N(47)–V(2)–N(57)	85.0(2)
N(17)–V(1)–N(37)	89.4(2)	N(47)–V(2)–N(67)	89.3(2)
N(27)–V(1)–N(37)	152.5(3)	N(57)–V(2)–N(67)	152.5(2)
V(1)–O(3)–S(1)	131.1(3)	V(2)–O(4)–S(1)	128.8(3)
O(3)–S(1)–O(4)	106.4(3)	O(4)–S(1)–O(5)	107.7(3)
O(3)–S(1)–O(5)	110.4(3)	O(4)–S(1)–O(6)	110.1(3)
O(3)–S(1)–O(6)	107.4(3)	O(5)–S(1)–O(6)	114.6(4)
N(37)–C(36)–C(66)–N(67)	79.7(9)		

Results and discussion

Synthesis. In the preparation of btpa the method of Dürr[7] was easily scaled up, and the method described here is similar using CH_3CN as solvent and Na_2CO_3 as base in the reaction of 6,6′-bis(bromomethyl)-2,2′-bipyridine with two equivalents of bis(2-pyridylmethyl)amine (Scheme 1) in reasonable yield. The highly colored impurities that usually form in this type of reactions were difficult to remove by simple recrystallizations of the product, but they were conveniently removed by complexation with copper(II) followed be decomplexation. In this way use of column chromatography in the work up was unnecessary.

Description of structures

Compound **1**. The dimeric cation which is shown in Fig. 1 is centrosymmetric. Each copper atom is bound to three nitrogen atoms of the btpa ligand, which links the copper atoms, and to one oxygen atom of the sulfato group, giving a square planar coordination. The Cu–N distances are 1.979(8) and 1.987(9) Å, respectively, for the pyridyl



Scheme 1. Synthesis of btpa.

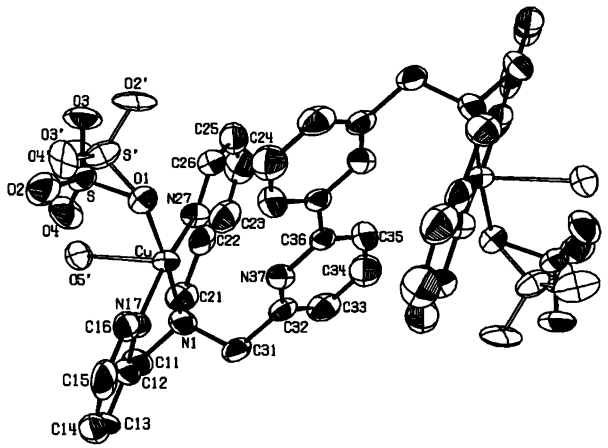


Fig. 1. Perspective ORTEP drawing of complex unit of **1** (50% probability ellipsoids). The numbering of the atoms (parentheses have been omitted for clarity). The atoms with the lowest occupation factors are drawn unshaded.

groups and 2.018(9) for the tertiary nitrogen. The Cu–O(1) distance is 1.940(7) Å. A very distorted octahedron is completed by N(37), Cu···N = 2.737(8) Å and by O(4) of the sulfato group, Cu···O = 2.662(11) Å. The distance between the two copper atoms of the dimer is 7.718(4) Å. However, the structure is disordered with some of the copper atoms being hydrated. O(5′) coordinates to copper, instead of O(4), at one of the apical positions, Cu···O(5′) = 2.48(2) Å. The sulfato group is bent about

O(1) so as to move it out of the way of O(5′). If the space group is centrosymmetric then the cations are also centrosymmetric, i.e. anhydrous or diaquo, the existence of monoaquo complexes would imply the existence of acentric domains in the crystal or a lower symmetry space group. Refinement in the space group $P\bar{1}$ was considered impractical, since the closeness of the structure to centrosymmetry, together with the relatively small number of reflections, would give unmanageably large correlations between parameters. The structure was therefore assumed to be centrosymmetric, which implies that the rings of the bipyridyl group are coplanar and the torsion angle N(37)–C(36)–C(36^{i})–N(37^{i}) is 180°.

Compound **2**. The dimeric cation which is shown in Fig. 2 has approximate two-fold symmetry. The vanadium atoms are coordinated octahedrally to four nitrogen atoms of the btpa group, one oxygen atom of a sulfato group and one oxygen atom. The two vanadium atoms are linked by the btpa group and by a sulfato bridge. The oxygen atoms of the sulfato bridge are located *cis* to the tertiary nitrogen atoms. The V = O distances are 1.586(5) and 1.590(5) Å. The V–O distances are 1.970(5) and 1.993(5) Å, V–N distances 2.096(6) to 2.147(7) Å [mean value 2.122(3) Å] for the pyridyl groups and 2.270(6) and 2.271(6) (Å) to the tertiary nitrogen atoms. The vanadium–vanadium distance is 4.328(2) Å. The bipyridyl group is twisted about the central bond so that the torsion angle N37–C36–C66–N67 is 79.7(9)°. The coordination octahedra are somewhat distorted, the root mean-square deviations from ideality[14] being 10.2 and 9.9°, respectively, strain in the ligand pulling the pyridyl nitrogen atoms away from the vanadyl oxygen atoms. Concerning other examples in the literature of sulfato bridged oxovanadium(IV) dimers, it should be mentioned that various aquated forms of $VOSO_4 \cdot nH_2O$ have been shown to contain sulfato bridges.[15–17] Wieghardt[18] has reported the preparation of $[(VO)_2(\mu\text{-}OH)(\mu\text{-}SO_4)(tacn)_2]I$ (tacn = 1,4,7-triazacyclononane). No crystal structure was reported, but the presence of bridging sulfate was based on IR spectroscopy.

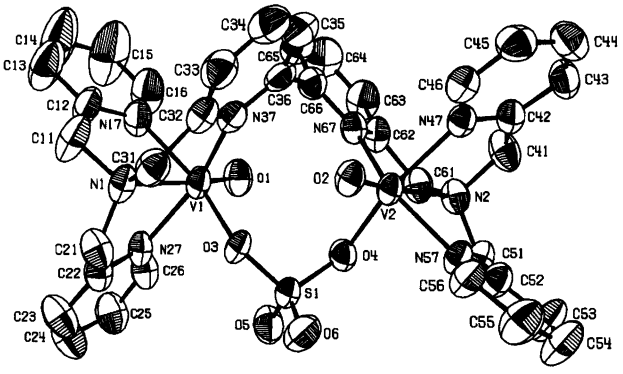


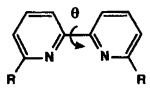
Fig. 2. Perspective ORTEP drawing of the cation in **2** (50% probability ellipsoids). The numbering of the atoms (parentheses have been omitted for clarity).

Magnetism. No magnetic coupling was observed in **1** and **2**. The absence of a bridging ligand and the long metal–metal distance in **1** explains this, and in the case of **2** the bridging sulfato group is a poor mediator of magnetic exchange.

UV–visible spectra. The optical absorption spectrum of btpa in methanol consists of several maxima, and it is close to the sum of the spectra of 6,6′-dimethyl-2,2′-bipyridine and 2-methylpyridine. The maxima at 246 and 288 nm are attributed to the bipyridine chromophore and the maxima at 261 and 267 nm to the pyridine chromophores. The optical absorption spectrum of **1** consists of several bands. The two bands at 829 and 691 nm are assigned as d–d bands, and the bands at 285 and 257 nm are assigned as transitions in the bipyridine and pyridine chromophores, respectively. The optical absorption spectrum of **2** consists of two d–d bands at 742 and 566 nm, a band at 366 nm, which is assigned as a vanadyl–oxygen to a vanadium charge transfer band and a pyridine-centered transition at 260 nm. The two d–d bands are rather intense, probably owing to a gain in intensity from the charge transfer-band. The almost perpendicular orientation of the pyridine groups in the bipyridine group reflected in the torsion angle N(37)–C(36)–C(66)–N(67) being 79.7° has the consequence that the transition at 285 nm attributed to the bipyridine group is absent.

Conclusions

A key point in the structures of the complexes **1** and **2** is the torsion angles (θ) N(37)–C(36)–C(36^{i})–N(37^{i}) and N(37)–(36)–C(66)–N(67), which were found to be 180 and 79.7(9)°, respectively, resulting in a metal–metal distance of 7.718(4) and 4.328(2) Å, respectively. In compound **2** resonance energy in the bipyridine unit is lost



owing to the almost perpendicular orientation of the pyridine groups. In this context the most interesting θ values are in the range 50–80°, since that results in metal–metal distances (3.0–4.3 Å) suitable for the coordination of one or two bridging ligands. To get an estimate of the energy needed for a rotation along the central bond in the bipyridine unit we can compare with bipyridine. In this case several calculations[19–21] reveal that conformations with θ values in the range 50–80° are 21–28 kJ mol^{-1} higher in energy than the θ = 180° conformation. Apart from this electronic effect others, such as steric effects, cannot be ruled out, and in btpa complexes steric effects must favor the θ = 180° conformation. In the case of **2** we see that the energy gain by forming a sulfato bridge more than compensates for the opposing electronic and steric effects. Taking into account the poor coordinating ability

of the sulfate ion, future prospects with respect to preparing bridged dimers containing other bridging ligands such as OH^-, N_3^- or O_2^{2-} look promising, and our current activities are following that direction.

Acknowledgements. We are indebted to Karen Jørgensen, University of Copenhagen, for copper analyses. A. H. is indebted to the Carlsberg Foundation and to the Danish Natural Science Research Council for the diffractometer.

References

1. Toftlund, H., Larsen, S. and Murray, K. S. *Inorg. Chem. 30* (1991) 3964.
2. Hodgson, D. J., Zietlow, M. H., Pedersen, E. and Toftlund, H. *Inorg. Chim. Acta 149* (1988) 111.
3. Ménage, S., Zang, Y., Hendrich, M. P. and Que, L. *J. Am. Chem. Soc. 114* (1992) 7786.
4. Oshio, H., Ino, E., Mogi, I. and Ito, T. *Inorg. Chem. 32* (1993) 5697.
5. Towle, D. K., Botsford, C. A. and Hodgson, D. J. *Inorg. Chim. Acta 141* (1988) 167.
6. Kitajima, N. and Moro-oka, Y. *Chem. Rev. 94* (1994) 737.
7. Dürr, H., Zengerle, K. and Trierweiler, H. P. *Z. Naturforsch., Teil B 43* (1988) 361.
8. Rodriguez-Ubis, J. C., Béatrice, A., Plancherel, D. and Lehn, J. M. *Helv. Chim. Acta 67* (1984) 2264.
9. SIR92. Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. and Camalli, M. *J. Appl. Crystallogr. 27* (1994) 435.
10. Busing, W. R., Martin, K. O. and Levy, H. A. *ORLFS. Report ORNL-TM-305*, Oak Ridge National Laboratory, Tennessee 1962.
11. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
12. Josephsen, J. and Pedersen, E. *Inorg Chem. 16* (1977) 2534.
13. Pedersen, E. *Acta Chem. Scand. 26* (1972) 333.
14. Hazell, A. *Acta Crystallogr., Sect. C 44* (1988) 1362.
15. Ladwig, G. *Z. Anorg. Allg. Chem. 364* (1969) 225.
16. Théobald, F. and Galy, J. *Acta Crystallogr., Sect. B 29* (1973) 2732.
17. Tachez, M. and Théobald, F. *Acta Crystallogr., Sect. B 36* (1980) 2873.
18. Wieghardt, K., Bossek, U., Volckmar, K., Swiridoff, W. and Weiss, *J. Inorg. Chem. 23* (1984) 1387.
19. Carlos, J. and Font, J. *J. Org. Chem. 55* (1990) 2637.
20. Yagi, M., Kazuhiro, M., Ohnuki, A., Suzuki, K., Higuchi, J. and Nagase, S. *Bull. Chem. Soc. Jpn. 58* (1985) 252.
21. Agresti, A., Bacci, M., Castellucci, E. and Salvi, P. R. *Chem. Phys. Lett. 89* (1982) 324

Received April 1, 1995.