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Preparation and crystal structure of *fac*-[Mo(bpt)(CO)$_3$][bpt = 1,3-bis(2-pyridyl)-1-thiapropane]

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Abstract

The reaction of pyridine-2-thiol with 2-vinylpyridine under reflux conditions affords a new asymmetric thioether, 1,3-bis(2-pyridyl)-1-thiapropane (bpt), which reacts readily with [Mo(CO)$_3$(MeCN)$_3$] in MeCN to give *fac*-[Mo(bpt)(CO)$_3$]. The last compound has been characterised by heteronuclear NMR spectroscopy and by an X-ray crystal structure determination.

Key words: Molybdenum; Carbonyl; Crystal structure; Pyridine-thioether

1. Introduction

The presence of sulfur, along with oxygen and/or nitrogen, in the inner coordination spheres of the metals in a wide assortment of metalloproteins including nitrogenases [1], type 1 copper proteins [2], liver alcohol dehydrogenase [3] *etc.*, has prompted much of the recent growth in the study of transition metal complexes of sulfides, thiolates and thioethers. It has been found that even relatively simple ligands containing both sulfur and nitrogen can exhibit considerable versatility in their coordination chemistry. Thus pyridine-2-thiol can bind to one or two metals through sulfur alone, or through both sulfur and nitrogen to a single metal by means of a four-membered chelate ring, or act as a bridging ligand between two or three metal centres [4]. To date there do not appear to be any examples of monodentate coordination through the nitrogen alone, presumably because of the constraints imposed by the geometry of the ligand. With these observations in mind, we considered that pyridine-2-thiol should make a useful building block for the preparation of new thioether ligands with a related but broader based coordination chemistry.

It has long been known that nucleophiles such as thiolates can add to the β-carbon of the side chain in 2- and 4-vinylpyridine [5] and we have exploited this reaction to prepare the new asymmetric thioether 1,3-bis(2-pyridine)-1-thiapropane, bpt (Reaction 1).

Examples of such pyridine-thioether chelating ligands are surprisingly rare. Tridentate ligands of the py(CH$_2$)$_n$S(CH$_2$)$_n$py type ($n = 1$ or 2) have received some attention, particularly for their relevance to type 1 copper proteins [2], but no crystal structures of their complexes have been reported so far, whilst Newkome *et al.* [6] have described nickel(II) and copper(II) complexes of penta- and hexadentate ligands based on pyridine and/or 2,2′-bipyridine connected via –CH$_2$-SCH$_2$– linkages. In this paper we describe the preparation and characterisation of a molybdenum(0) complex of bpt, [Mo(bpt)(CO)$_3$].

2. Results and discussion

Bpt was obtained in good yield according to Reaction 1. The ^{1}H and ^{13}C NMR spectra of bpt both show pairs of triplets characteristic of the –CH$_2$CH$_2$– linkage, in addition to complicated sets of resonances in the aromatic region from the two different 2-substituted pyridines. The natural-abundance ^{15}N NMR spectrum shows signals at −63.2 and −75.6 ppm (rela-

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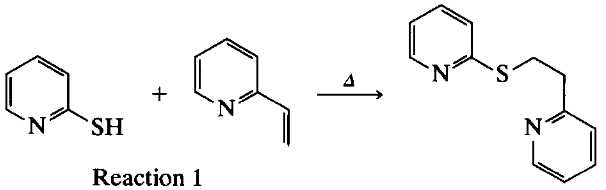


Reaction 1

tive to nitromethane), both of which appear as doublets by virtue of coupling to the *ortho*-hydrogen; the $^2J_{NH}$ values of 11 Hz in both cases are as expected [7].

The IR spectrum of bpt is typical of substituted pyridines [8]; upon coordination most of the bands are shifted by up to 30 cm^{-1}, but there is little of specific diagnostic value [the ν(C–S) modes, which are expected to be weak, are obscured by strong pyridine bands]. By far the strongest features in the IR spectrum of [Mo(bpt)(CO)$_3$] are the two ν(C=O) modes at 1907 and 1784 cm^{-1}, consistent with the facial arrangement of the carbonyl ligands (molecular models suggest that bpt could adopt a meridional geometry only with difficulty). The positions of the carbonyl stretches are intermediate between those for *fac*-[Mo(CO)$_3$(py)$_3$] [9] (py = pyridine; 1896 and 1754 cm^{-1}) and *fac*-[Mo(CO)$_3$(ttn)] [10] (ttn = 2,5,8-trithianonane; 1919 and 1810 cm^{-1}; all the values are for KBr pellet spectra). The ^{95}Mo NMR data show a similar trend, thus [Mo(bpt)(CO)$_3$] gives a singlet at −1114 ppm (in CD$_3$CN relative to external 2M Na$_2$MoO$_4$), compared to resonances at −800 ppm for [Mo(CO)$_3$(py)$_3$] [12] and −1213 ppm for [Mo(CO)$_3$(ttn)] [10]. The ^{14}N NMR spectrum of [Mo(bpt)(CO)$_3$] shows only one peak, at −69 ppm (linewidth *ca.* 70 Hz), suggesting that the signals from the two nitrogens become coincident upon coordination.

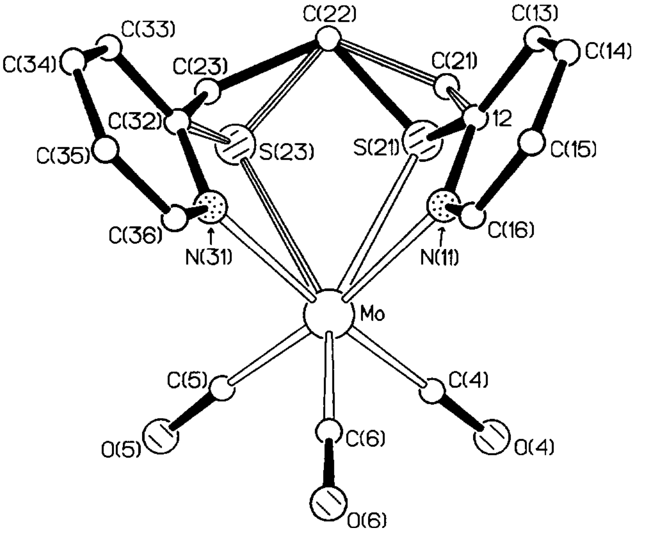


Fig. 1. Molecular structure of [Mo(bpt)(CO)$_3$], showing the atomic numbering scheme. The two enantiomers (disordered in the crystal) are shown, one having the bridging atoms S(21), C(22) and C(23) in the bpt bridge, the second having C(21), C(22) and S(23); the other atoms are common to both enantiomers.

TABLE 1. Final atomic coordinates (fractional × 10^4) for *fac*-[Mo(bpt)(CO)$_3$]

Atom	x	y	z	SOF [a]
Mo	2698.9(5)	−342.4(4)	1421.1(4)	
N(11)	1257(5)	446(5)	1051(4)	
C(12)	373(6)	−30(5)	1165(4)	
C(13)	−569(7)	403(7)	1038(5)	
C(14)	−589(9)	1333(8)	791(6)	
C(15)	321(9)	1793(7)	694(6)	
C(16)	1211(8)	1340(6)	819(6)	
S(21)	806(4)	−1164(3)	1439(3)	0.490(8)
C(21)	242(17)	−1026(11)	1472(9)	0.510(8)
C(22)	378(6)	−1213(6)	2409(5)	
S(23)	1685(3)	−1157(3)	2635(3)	0.510(8)
C(23)	1361(13)	−1044(10)	2999(11)	0.490(8)
N(31)	2324(5)	437(4)	2556(4)	
C(32)	1754(6)	−40(5)	3075(5)	
C(33)	1443(7)	352(6)	3775(5)	
C(34)	1723(8)	1267(6)	3945(5)	
C(35)	2308(7)	1749(6)	3425(6)	
C(36)	2579(7)	1322(6)	2736(6)	
C(4)	2884(6)	−1097(6)	487(6)	
O(4)	3006(5)	−1567(5)	−62(4)	
C(5)	3809(8)	−1081(6)	1856(5)	
O(5)	4493(6)	−1531(5)	2087(4)	
C(6)	3694(6)	482(6)	995(4)	
O(6)	4312(5)	994(4)	733(4)	

[a] Site occupancy factor, if less than 1.0.
Esds are in parentheses.

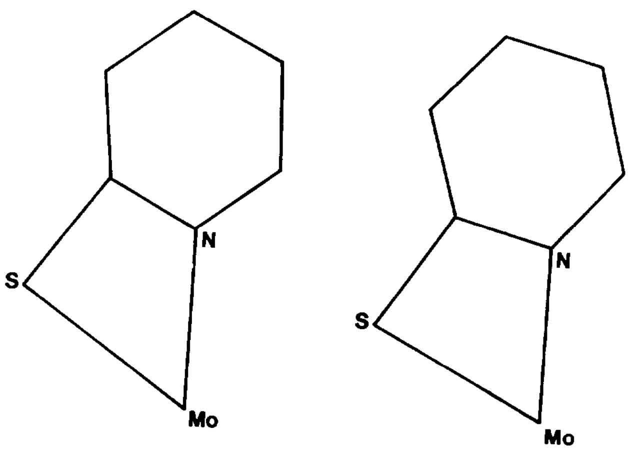
The X-ray crystal structure of [Mo(bpt)(CO)$_3$] is shown in Fig. 1; atomic coordinates are in Table 1 and bond dimensions are in Table 2. The molybdenum is in a distorted octahedral environment, with the principal distortion arising from the asymmetry imposed by the 4- and 6-membered chelate rings of the bpt ligand. This has the effect of displacing the sulfur atom away from the site opposite the carbonyl group of C(6). The asymmetry of the ligand means that the complex is chiral; the crystal exhibits disorder and is, in fact, a random mixture of the two enantiomers, in approximately equal proportions, related by a pseudo-mirror plane through the Mo, C(6) and C(22) atoms. The pyridine rings and C(22) are common to both enantiomers but the other atoms of the -SCH$_2$CH$_2$- bridge have alternative sites according to the direction of the group.

It is interesting to compare the geometry of the four-membered chelate ring of bpt with those found in pyridine-2-thiolate complexes. In Fig. 2 the geometries of this fragment from [Mo(bpt)(CO)$_3$] (**1**) and from [MoH(PyS)$_2$(tipt)(PEtPh$_2$)] (**2**) (PySH = pyridine-2-

TABLE 2. Molecular dimensions

(a) About the Mo atom			
Mo–N(11)	2.279(6)	Mo–C(4)	1.923(9)
Mo–S(21)	2.734(5)	Mo–C(5)	1.934(10)
Mo–S(23)	2.701(5)	Mo–C(6)	1.892(8)
Mo–N(31)	2.267(6)		
N(11)–Mo–S(21)	57.6(2)	S(21)–Mo–C(5)	116.3(3)
N(11)–Mo–S(23)	90.7(2)	S(23)–Mo–C(5)	81.2(3)
S(21)–Mo–S(23)	50.6(1)	N(31)–Mo–C(5)	96.0(3)
N(11)–Mo–N(31)	79.3(2)	C(4)–Mo–C(5)	85.2(4)
S(21)–Mo–N(31)	90.2(2)	N(11)–Mo–C(6)	99.2(3)
S(23)–Mo–N(31)	57.3(2)	S(21)–Mo–C(6)	152.8(2)
N(11)–Mo–C(4)	98.8(3)	S(23)–Mo–C(6)	153.0(2)
S(21)–Mo–C(4)	83.4(2)	N(31)–Mo–C(6)	99.8(3)
S(23)–Mo–C(4)	116.5(2)	C(4)–Mo–C(6)	86.8(3)
N(31)–Mo–C(4)	173.3(3)	C(5)–Mo–C(6)	88.0(3)
N(11)–Mo–C(5)	172.0(3)		
(b) In the bpt ligand			
N(11)–C(12)	1.351(10)	C(22)–S(23)	1.751(8)
N(11)–C(16)	1.330(10)	C(22)–C(23)	1.643(13)
C(12)–C(13)	1.392(11)	S(23)–C(32)	1.753(7)
C(12)–S(21)	1.768(8)	C(23)–C(32)	1.520(13)
C(12)–C(21)	1.515(13)	C(32)–N(31)	1.334(9)
C(13)–C(14)	1.384(12)	C(32)–C(33)	1.368(10)
C(14)–C(15)	1.366(13)	N(31)–C(36)	1.334(11)
C(15)–C(16)	1.345(13)	C(36)–C(35)	1.359(12)
S(21)–C(22)	1.733(8)	C(35)–C(34)	1.351(12)
C(21)–C(22)	1.615(14)	C(34)–C(33)	1.380(11)
Mo–N(11)–C(12)	115.0(5)	S(21)–C(22)–C(23)	108.4(8)
Mo–N(11)–C(16)	125.9(6)	Mo–S(23)–C(22)	109.4(3)
C(12)–N(11)–C(16)	118.7(7)	Mo–S(23)–C(32)	84.9(3)
N(11)–C(12)–C(13)	120.9(7)	C(22)–S(23)–C(32)	100.6(4)
N(11)–C(12)–S(21)	102.6(6)	C(22)–C(23)–C(32)	116.9(10)
C(13)–C(12)–S(21)	136.5(7)	S(23)–C(32)–N(31)	102.0(6)
N(11)–C(12)–C(21)	127.7(10)	C(23)–C(32)–N(31)	127.4(10)
C(13)–C(12)–C(21)	111.4(11)	S(23)–C(32)–C(33)	136.0(7)
C(12)–C(13)–C(14)	118.9(9)	C(23)–C(32)–C(33)	110.7(11)
C(13)–C(14)–C(15)	118.4(9)	N(31)–C(32)–C(33)	121.9(7)
C(14)–C(15)–C(16)	120.3(10)	Mo–N(31)–C(32)	115.5(5)
N(11)–C(16)–C(15)	122.8(9)	Mo–N(31)–C(36)	126.7(6)
Mo–S(21)–C(12)	84.2(3)	C(32)–N(31)–C(36)	117.8(7)
Mo–S(21)–C(22)	108.6(3)	N(31)–C(36)–C(35)	123.4(9)
C(12)–S(21)–C(22)	100.4(4)	C(36)–C(35)–C(34)	118.6(8)
C(12)–C(21)–C(22)	118.4(11)	C(35)–C(34)–C(33)	119.3(8)
C(21)–C(22)–S(23)	108.3(9)	C(32)–C(33)–C(34)	119.0(8)
(c) In the carbonyl ligands			
C(4)–O(4)	1.154(9)	Mo–C(4)–O(4)	178.3(8)
C(5)–O(5)	1.166(10)	Mo–C(5)–O(5)	177.2(8)
C(6)–O(6)	1.172(8)	Mo–C(6)–O(6)	179.7(3)
(d) Torsion angles in the bpt ligand			
N(11)–C(12)–S(21)–C(22)	114.1(6)		
C(13)–C(12)–S(21)–C(22)	−68.1(10)		
C(12)–S(21)–C(22)–C(23)	−103.6(8)		
S(21)–C(22)–C(23)–C(32)	75.7(12)		
C(22)–C(23)–C(32)–N(31)	−76.7(15)		
C(22)–C(23)–C(32)–C(33)	103.3(12)		
N(31)–C(32)–S(23)–C(22)	−113.6(6)		
C(33)–C(32)–S(23)–C(22)	71.7(10)		
C(32)–S(23)–C(22)–C(21)	103.3(8)		
S(23)–C(22)–C(21)–C(12)	−74.2(13)		
C(22)–C(21)–C(12)–N(11)	76.4(15)		
C(22)–C(21)–C(12)–C(13)	−100.4(13)		

Bond lengths, Å; angles, deg; Esds are in parentheses.



(1) (2)

Fig. 2. Comparison of the C_5H_4NSMo moieties from [Mo(bpt)(CO)$_3$] (1) and [MoH(PyS)$_2$(tipt)(PEtPh$_2$)] (2). The figure is drawn such that the Mo–N vectors are parallel.

thiol, tiptH = 2,4,6-triisopropylthiophenol) [12], a fairly typical molybdenum pyridine-2-thiolate complex, are compared. The nitrogen in **1** has a geometry which is closer to trigonal than that in **2** [mean Mo–N–C angles for the two enantiomers are 115.3(3) and 126.3(4) in **1**, compared to average values of 102.9(6)° and 138.0(9)° in **2**], largely at the expense of the sulfur-bearing carbon atoms of the pyridine rings [mean S–C–N and S–C–C angles of 102.3(3)° and 136.3(3)° respectively in **1** compared to averages of 110.1(12)° and 128.5(10)° in **2**]. The reasons for this 'straightening out' of the pyridine moiety in going from thiolate to thioether chelation are not immediately obvious, and invite further study. The bite angle of the four-membered chelate ring of bpt [the mean value for the two enantiomers is 57.5(2)°], falls below the usual range of 64–67° for pyridine-2-thiolate complexes [4,12], whilst the Mo–S bond in **1**, mean value 2.717(17) Å, is rather long (molybdenum–thioether bond lengths are typically 2.50–2.65 Å). However the crystallographic disorder in **1** could affect these parameters.

In addition to studies on molybdenum and vanadium, we are currently investigating the coordination chemistry of bpt and related ligands with copper, with a view to modelling the type 1 centres of nitrite reductases [2].

3. Experimental section

All chemicals were purchased from Aldrich and used as received. Solvents were dried by standard procedures and redistilled under nitrogen. Preparations and manipulations were carried out under nitrogen by standard Schlenk techniques.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer. ^{1}H, ^{13}C, ^{14}N, ^{15}N and ^{95}Mo NMR spectra were recorded at 270.17, 67.94, 19.52, 27.38 and 17.06 MHz respectively on a Jeol GSX270 spectrometer. ^{1}H and ^{13}C chemical shifts are quoted relative to tetramethylsilane, ^{14}N and ^{15}N shifts relative to nitromethane and ^{95}Mo shifts relative to 2M Na_2MoO_4.

3.1. Preparation of 1,3-bis(2-pyridine)-1-thiapropane, bpt

To a solution of pyridine-2-thiol (7.07 g, 64 mmol) in toluene (200 ml) was added 2-vinylpyridine (6.82 ml, 63 mmol). The solution was boiled under reflux for 4 h, and the solvent then distilled off at atmospheric pressure. The dark red liquid residue was distilled under reduced pressure to give 1,3-bis(2-pyridine)-1-thiapropane as a yellow liquid. Yield 12.0 g, 88%. B.p. 145–150°C/6 mmHg.

Density *ca.* 1.1 g cm^{-3}. Infrared spectrum (thin liquid film, KBr plates): 1579s, 1453m, 1416s, 1283w, 1126s, 1047w, 987w, 758s, 620w and 480w. ^{1}H NMR (CD_2Cl_2): δ 3.18 (t, 2H, $^{3}J_{HH}$ 7.4, CH_2S), 3.58 (t, 2H, $^{3}J_{HH}$ 7.4, $CH_2C_5H_4N$), 6.95–7.62 (m, 6H, 3,4,5-C_5H_4N) and 8.42–8.55 (m, 2H, 6-C_5H_4N). ^{13}C NMR (CD_2Cl_2): δ 29.1 (t, $^{1}J_{CH}$ 142.1, CH_2S), 37.8 (t, $^{1}J_{CH}$ 129.3, $CH_2C_5H_4N$), 119.2 (d, $^{1}J_{CH}$ 145.5, 5-C_5H_4N), 121.3 (d, $^{1}J_{CH}$ 143.9, 5-C_5H_4N), 121.9 (d, $^{1}J_{CH}$ 166.5, 3-C_5H_4N), 123.0 (d, $^{1}J_{CH}$ 161.7, 3-C_5H_4N), 135.8 (d, $^{1}J_{CH}$ 163.1, 4-C_5H_4N), 136.0 (d, $^{1}J_{CH}$ 161.0, 4-C_5H_4N), 149.2 (d, $^{1}J_{CH}$ 176.8, 6-C_5H_4N), 149.3 (d, $^{1}J_{CH}$ 178.7, 6-C_5H_4N), 158.8 (s, 2-C_5H_4N), 159.9 (s, 2-C_5H_4N). ^{15}N NMR (neat), δ −75.6 (d, $^{2}J_{NH}$ 11), −63.2 (d, $^{2}J_{NH}$ 11).

3.2. Preparation of [1,3-bis-(2-pyridine)-1-thiapropane] tricarbonylmolybdenum(0)

Acetonitrile (20 ml) was added to Mo(CO)$_6$ (0.53 g, 2 mmol) and the mixture was boiled under reflux for 3 h. To the resulting yellow solution of [Mo(CO)$_3$(MeCN)$_3$] was added a solution of 1,3-bis-(2-pyridine)-1-thiopropane (0.44 g, 2 mmol) in MeCN (10 ml). The mixture was stirred overnight at room temperature, then filtered. The filtrate was concentrated to dryness *in vacuo*, and the resulting solid was stirred thoroughly with Et_2O, then filtered off and dried *in vacuo*. Yield 0.43 g, 54%.

Infrared spectrum (KBr pellet): 1907vs, 1812sh, 1784vs, 1601w, 1473w, 1445m, 1265w, 1160m, 778m, 629w and 510w. ^{1}H NMR (CD_2Cl_2): δ 3.39 (m, 4H, CH_2CH_2), 6.99–7.83 (m, 6H, 3,4,5-C_5H_4N) and 8.51–8.88 (m, 2H, 6-C_5H_4N). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ

34.0 (s, CH_2S) and 41.4 (s, $CH_2C_5H_4N$). ^{14}N NMR (acetone): δ −69. ^{95}Mo NMR (CD_3CN): δ −1114.

3.3. X-ray structure determination of [Mo(bpt)(CO)$_3$]

Slow diffusion of layered Et_2O over a solution of [Mo(bpt)(CO)$_3$] in acetone at room temperature produced brown rectangular plate-shaped crystals. One of these, dimensions 0.20 × 0.18 × 0.036 mm, was mounted on a glass fibre, in air. After preliminary photographic examination, the crystal was transferred to our Enraf-Nonius CAD4 diffractometer (with monochromated radiation).

Crystal data: $C_{15}H_{12}MoN_2O_3S$, M = 396.3. Orthorhombic, space group *Pcab* (equiv. to no. 61), $a = 13.064(1)$, $b = 14.1909(6)$, $c = 16.900(1)$ Å, $U = 3133.0$ Å^3. $Z = 8$, $D_c = 1.680$ g cm^{-3}, $F(000) = 1584$, μ(Mo-$K\alpha$) = 9.6 cm^{-1}, λ(Mo$K\alpha$) = 0.71069 Å. Accurate cell dimensions were determined by refinement from the centred settings of the five strongest reflections having $\theta = 10$–$11°$ and their symmetry equivalents, each measured in four orientations. Intensities of 2753 unique reflections were measured to $\theta_{max} = 25°$. Corrections for Lorentz-polarisation effects, slight deterioration (4% overall) and absorption (analytically calculated) were applied.

The structure was solved by the heavy atom method in the SHELX program [13]. Refinement was by full-matrix least-squares methods. Except for the disordered C-atoms, all the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the pyridine rings were included in idealised positions; their isotropic thermal parameters were allowed to refine freely. The refinement converged at $R = 0.081$ and $R_w = 0.063$ [13] for 2165 reflections (those with $I > \sigma_I$) weighted $w = (\sigma_F^2 + 0.00030F_0^2)^{-1}$. In the final difference map, the only peaks above the background noise level were *ca.* 0.8 eÅ^{-3} and close to the carbon atoms of the disordered bridging group.

The structure determination and the refinement process were carried out with crystallographic programs listed above and in Table 4 of reference 14, using a MicroVAX II machine. The scattering factors for neutral atoms were taken from the "International Tables for X-ray Crystallography" [15]. Tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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