

a chelating ligand as opposed to a monodentate ligand. The nature of the polymer backbone could be important, depending on the stabilizing ligand chosen. It is also possible to regenerate at least 40% of the original amount of  $\text{LiCuR}_2$  on the polymer after it has been reacted with an organic substrate. Immobilizing organocopper compounds on polymeric supports bearing a suitable stabilizing ligand L has value despite the leaching problem as it ultimately affords organocopper species that have considerably longer lifetimes and can be reacted at higher temperatures than the in situ prepared species.

We are extending our studies to the reactions of the immobilized organocopper compounds to other organic substrates like  $\alpha,\beta$ -unsaturated carbonyls, vinyl halides, and epoxides to demonstrate the stereospecific reactivities of the immobilized species. We are also investigating other stabilizing ligands in order to minimize the leaching problem and organocopper compounds to extend the usefulness of this procedure for their stabilization and isolation. Structural characterization of the immobilized species by infrared ( $4000\text{--}150\text{ cm}^{-1}$ ) and multinuclear solid-state NMR spectroscopy are also in progress.

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**Registry No.** 1-Iodoctane, 629-27-6; nonane, 111-84-2; dodecane, 112-40-3.

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### Synthesis and Characterization of $\text{Mo}(\text{nor})_4$ (nor = 1-Norbornyl)

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There is a good possibility that dinitrogen binds to a  $\text{Mo}(\text{IV})$  center in nitrogenase at some point during the process of being reduced to ammonia.<sup>1</sup> For this reason we have been interested in preparing monomeric  $d^2$  complexes of the type  $\text{MX}_4$  ( $\text{M} = \text{Mo}, \text{W}$ ). We were encouraged that dinitrogen would bind to  $\text{Mo}(\text{IV})$  or  $\text{W}(\text{IV})$  by the fact that  $[\text{W}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]_2(\mu\text{-N}_2)$ , formally a dinitrogen complex with  $\text{W}(\text{IV})$  at each end,<sup>2</sup> can be prepared in high yield by reducing  $\text{W}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3(\text{CF}_3\text{SO}_3)$  under  $\text{N}_2$ .<sup>3</sup> Although complexes of the type  $\text{MX}_4$  where X is a bulky phenoxide ( $\text{M} = \text{W}$ )<sup>4</sup> or thiolate ( $\text{M} = \text{Mo}, \text{W}$ )<sup>5</sup> ligand have been prepared, none binds dinitrogen to any observable extent, perhaps in part because both alkoxide and thiolate<sup>6</sup> ligands are (to varying degrees) good  $\pi$ -electron donors. Therefore, we decided to explore  $\text{MX}_4$  complexes in which X is an alkyl ligand. At least we might be able to use an  $\text{MoR}_4$  species as a starting material for the preparation of monomeric molybdenum phenoxide complexes, still

unknown species, in order to compare them with the analogous tungsten species.

$\text{MR}_4$  complexes where  $\text{M} = \text{Mo}$  or  $\text{W}$  are rare.  $\eta^3$ -Allyl<sup>7</sup> and benzyl<sup>8</sup> complexes are known for both  $\text{Mo}$  and  $\text{W}$ , but neither the allyl nor the benzyl ligand is likely to be unidentate.  $\text{Mo}(\text{mesityl})_4$ <sup>9</sup> has been reported, although it was not characterized thoroughly, and so far we have not been able to reproduce the reported preparation. We felt that R should not be susceptible to decomposition reactions based on  $\beta$ - or  $\alpha$ -hydrogen abstraction reactions,<sup>10</sup> a restriction that severely limits the possible choices of R.

In 1972 Bower and Tennent reported a series of tetra-1-norbornyl complexes containing first-row transition metals plus Zr and Hf.<sup>11</sup> Their stability was attributed to the fact that  $\beta$  elimination would produce a high-energy bridgehead olefin.  $\text{Cr}(\text{nor})_4$  was reported to have a half-life of 7.6 h at 250 °C and to be stable indefinitely in 0.1 M  $\text{H}_2\text{SO}_4$ . It did not react with pyridine or several other small molecules. Since the ionic radius of molybdenum is  $\sim 0.12\text{ \AA}$  larger than that of chromium, we thought it possible that the analogous  $\text{Mo}(\text{nor})_4$  complex might display greater reactivity toward small substrates. This note describes the synthesis and physical properties of  $\text{Mo}(\text{nor})_4$ .

### Experimental Section

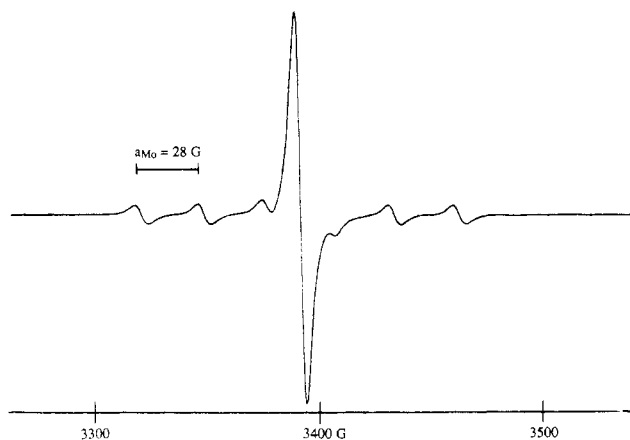
All operations were performed under nitrogen in a Vacuum Atmospheres drybox or by standard Schlenk or vacuum-line techniques. All solvents were dried and freshly distilled under nitrogen prior to use.  $\text{MoCl}_3(\text{THF})_3$ <sup>12</sup> and 1-norbornyllithium<sup>13</sup> were prepared according to literature procedures.

EPR spectra were recorded on a Varian E-Line spectrometer. Electrochemical measurements were performed by using a Princeton Applied Research Model 173 potentiostat/galvanostat and Model 175 universal programmer in conjunction with a Houston Instruments RE-0089 X-Y recorder. Cyclic voltammograms were obtained in the drybox in dichloromethane (dried and distilled) containing  $\sim 0.1\text{ M}$   $[\text{n-Bu}_4\text{N}]^+\text{PF}_6^-$ .  $E_{1/2}$  values are referenced to  $\text{Ag}/\text{Ag}^+$  and uncorrected for junction potentials. Mass spectra were obtained on a Finnigan Mat 8200 spectrometer operating at low resolution. Magnetic susceptibility was determined in toluene- $d_8$  by the Evans technique.<sup>14</sup> A diamagnetic correction of  $-313.92 \times 10^{-6}\text{ cgsu mol}^{-1}$  was calculated using Pascals constants.<sup>15</sup> The mass susceptibility of toluene- $d_8$  was approximated by using the measured value for toluene- $d_0$  of  $-0.7176 \times 10^{-6}\text{ cgsu g}^{-1}$ .<sup>16</sup>

**Preparation of  $\text{Mo}(\text{nor})_4$ .**  $\text{MoCl}_3(\text{THF})_3$  (2.0 g, 4.8 mmol) was added rapidly to a vigorously stirred solution of 1-norbornyllithium (1.95 g, 19.1 mmol) in 50 mL of a mixture of THF and ether (1:30 by volume) at  $-46\text{ }^\circ\text{C}$ . As the reaction mixture was warmed to 25 °C, it became brown, then blue, and after  $\sim 90$  min red with a blue precipitate. The reaction mixture was filtered to remove the bulk of the blue solids, and the solvent was removed from the filtrate in vacuo. The resulting red-brown residue was extracted with toluene, and the extract was filtered to remove any remaining blue solids. The volume of the red filtrate was then reduced in vacuo to yield crystals of red  $\text{Mo}(\text{nor})_4$ . Two crops of red microcrystals totaling 550 mg (25%) were collected.  $\text{Mo}(\text{nor})_4$  can be purified further

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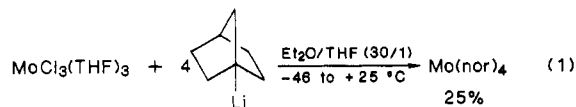


**Figure 1.** EPR (X-band) spectrum (295 K) of  $\text{Mo}(\text{nor})_4$  in toluene ( $g = 1.991$ ,  $a_{\text{Mo}} = 28$  G).

by sublimation at 130 °C and 0.001  $\mu\text{m}$  over a period of 72 h.  $\text{Mo}(\text{nor})_4$  also can be recrystallized from concentrated solutions of toluene by cooling to -46 °C overnight:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  -70, -48, -33, +10, +35, +58 (all signals very broad); EPR (toluene, 295 K) ( $g = 1.991$ ,  $a_{\text{Mo}} = 28$  G, half-width = 4 G (see Figure 1); EI mass spectrum  $m/e$  [ $\text{M} - \text{H}$ ] $^+$  476.9 amu. Anal. Calcd for  $\text{MoC}_{28}\text{H}_{44}$ : C, 70.56; H, 9.31; Cl, 0.0. Found: C, 70.33; H, 9.38; Cl,  $\leq 0.3$ .

### Results and Discussion

$\text{Mo}(\text{nor})_4$  was prepared as shown in eq 1. A blue precipitate was filtered off, and red crystalline  $\text{Mo}(\text{nor})_4$  was isolated from

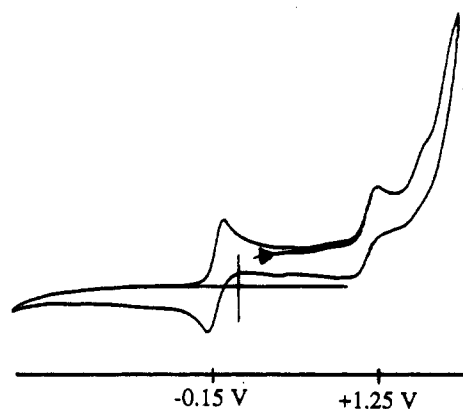


the filtrate.  $\text{Mo}(\text{nor})_4$  may be recrystallized from toluene or sublimed. The reaction shown in eq 1 proceeds poorly in pentane.

The blue material could not be characterized. It is extremely air and moisture sensitive, soluble only in coordinating solvents, and stable in the solid state for only a few days (it decomposes to a brown solid even when stored under nitrogen in the dark at -40 °C). It appears to be stable when dissolved in cold THF, although attempts to isolate a product by cation exchange or recrystallization have not yet been successful. On the basis of solubility and color, we suspect that the blue material is  $\text{Li}^+[\text{Mo}(\text{nor})_4]^-$ . Blue  $[\text{CrR}_4]^-$  complexes have been reported, and cation exchange was not successful.<sup>17</sup>  $\text{Cr}(\text{CH}_2\text{R})_4$  complexes ( $\text{R} = \text{CMe}_3$ ,  $\text{CMe}_2\text{Ph}$ ,  $\text{CPh}_3$ ,  $\text{SiMe}_3$ ) have been prepared by oxidizing the  $[\text{Cr}(\text{CH}_2\text{R})_4]^-$  species with air,<sup>17</sup> but we have not been able to oxidize the blue material to  $\text{Mo}(\text{nor})_4$ .  $[\text{Mo}(\text{nor})_4]^-$  may be oxidized by molybdenum under the reaction conditions, thereby accounting for the low yield of  $\text{Mo}(\text{nor})_4$ . The failure to obtain suitable yields of  $\text{Mo}(\text{nor})_4$  when the reaction is carried out in pentane could result from the inability of pentane to effectively stabilize the anion.

An attempted X-ray structure study showed that  $\text{Mo}(\text{nor})_4$  is isomorphous with tetrahedral  $\text{Co}(\text{nor})_4$ .<sup>18</sup> The structure could not be solved satisfactorily (although the  $\text{MoC}_4$  core appeared to be well-behaved) due to what is believed to be disorder of the norbornyl ligands beyond the  $\alpha$ -carbon atoms.  $\text{Co}(\text{nor})_4$  is also a severely disordered molecule that was solved by refining the norbornyl ligands as rigid groups. There appears to be no report of a structure study of a well-behaved  $\text{M}(\text{nor})_4$  complex. (Full details can be found in the supplementary material.)

$\mu_{\text{eff}}$  for  $\text{Mo}(\text{nor})_4$  was determined to be 2.62  $\mu_{\text{B}}$  (300 K) by the Evans method.<sup>14</sup> This value is slightly lower than  $\mu_{\text{eff}} = 2.84 \mu_{\text{B}}$



**Figure 2.** Cyclic voltammogram of  $\text{Mo}(\text{nor})_4$  in  $\text{CH}_2\text{Cl}_2$  referenced to  $\text{Ag}/\text{Ag}^+$  with 0.1 M  $[(n\text{-Bu})_4\text{N}]^+[\text{PF}_6]^-$  as supporting electrolyte. Scan speed is 200  $\text{mV s}^{-1}$ .

determined for  $\text{Cr}(\text{nor})_4$ , a value that is close to the spin-only value for two unpaired electrons.<sup>11</sup> A lower value is to be expected as a result of spin-orbit coupling in the heavier group 6 metal.<sup>19</sup>

Figure 1 displays the EPR spectrum of  $\text{Mo}(\text{nor})_4$  recorded in toluene at 295 K ( $g = 1.991$ ;  $a_{\text{Mo}} = 28$  G; half-width = 4 G). The resonance observed from  $\text{Mo}(\text{nor})_4$  is a rare example of a room-temperature EPR signal originating from a  $d^2$  metal center having two unpaired electrons residing in an  $e_g$  orbital and is probably due to the small zero-field effects present in this highly symmetric molecule. The EPR spectrum of  $\text{Cr}(\text{nor})_4$  in benzene ( $g = 1.986$ ; half-width = 21 G)<sup>20</sup> is similar to that of  $\text{Mo}(\text{nor})_4$ .

In spite of its paramagnetism,  $\text{Mo}(\text{nor})_4$  does display a  $^1\text{H}$  NMR spectrum. Six very broad peaks were observed at -70, -48, -33, 10, 35, and 58 ppm.

A cyclic voltammogram for  $\text{Mo}(\text{nor})_4$  obtained in dichloromethane is shown in Figure 2. Two oxidation waves at -0.15 and +1.25 V are observed. The oxidation at -0.15 V has peak separations ( $E_{\text{pc}} - E_{\text{pa}}$ ) of 120–170 mV over scan rates of 20–500  $\text{mV s}^{-1}$ . A plot of  $i_{\text{pc}}$  vs. the square of the scan rate gives a straight line in the range 20–500  $\text{mV s}^{-1}$ . In addition,  $i_{\text{pc}}/i_{\text{pa}} \approx 1$  in the same scan range. Therefore the -0.15 V oxidation process is reversible or nearly reversible on this time scale.<sup>21</sup> The irreversible wave at +1.25 V corresponds to a second oxidation of  $\text{Mo}(\text{nor})_4$ . This oxidation is clearly irreversible, even at 500  $\text{mV s}^{-1}$  scan speed. Unfortunately, attempts to chemically oxidize  $\text{Mo}(\text{nor})_4$  by  $\text{Ag}^+$  or ferrocenium so far have yielded no isolable products. These results should be compared with those for the analogous cobalt complex;  $[\text{Co}(\text{nor})_4]^+$  can be isolated.<sup>22</sup>

$\text{Mo}(\text{nor})_4$  is stable to oxygen but decomposes when exposed to moisture.  $\text{Mo}(\text{nor})_4$  does not react with pyridine, propylene oxide, 3-hexyne, 1 equiv of CO, or 2,6-dimethylphenol in refluxing toluene. It apparently decomposes to uncharacterizable products in the presence of a large excess of CO at room temperature overnight or in refluxing 2,6-dimethylphenol overnight. Therefore,  $\text{Mo}(\text{nor})_4$  appears to be more reactive than  $\text{Cr}(\text{nor})_4$ , although it is still unreactive on an absolute scale. Unfortunately, it does not appear even to serve as a source of  $\text{Mo}(\text{phenoxide})_4$ , a type of species whose tungsten analogues are known<sup>4</sup> but one which so far has not been prepared.

We conclude that the larger size of molybdenum(IV) versus chromium(IV) is not enough to allow  $\text{Mo}(\text{nor})_4$  to react readily with small molecules, certainly not dinitrogen to give  $[\text{Mo}(\text{nor})_4]_2(\mu\text{-N}_2)$ . Other strictly homoleptic alkyl complexes probably also either will be too crowded to form  $[\text{MoR}_4]_2(\mu\text{-N}_2)$  complexes

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or will decompose too rapidly. It may be possible to prepare a "MR'<sub>x</sub>R<sub>y</sub>" species by reduction of a M(V) complex (M = Mo or W; R' is a bulky, relatively innocuous ligand (e.g. mesityl), and R is methyl) that approaches the balance that apparently is achieved in "W( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Me<sub>3</sub>". We will continue to operate under the assumption that under the right circumstances alkyl ligands can provide an electronically favorable circumstance for dinitrogen to bind.

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**Registry No.** MoCl<sub>3</sub>(THF)<sub>3</sub>, 31355-55-2; Mo(nor)<sub>4</sub>, 115406-98-9; CO, 630-08-0; 1-norbornyllithium, 930-81-4; pyridine, 110-86-1; propylene oxide, 75-56-9; 3-hexyne, 928-49-4; 2,6-dimethylphenol, 576-26-1.

**Supplementary Material Available:** Experimental procedures, a table of crystallographic data, an ORTEP drawing, and listings of positional and anisotropic thermal parameters, general temperature factor expressions, bond distances for non-hydrogen atoms, and bond angles for non-hydrogen atoms (20 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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### Direct C-Cl...Ca<sup>2+</sup> Binding: Crystal Structure of Calcium Chloroacetate Hydrate

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Although carbon-bound halogen atoms (X = F, Cl, Br, I) are generally considered to be poor donors toward metal ions, there have been a number of recent reports of C-X...M coordination encompassing a broad range of structural environments and bond motifs.<sup>1-4</sup> Both "covalent" and "ionic" C-X...M interactions have been observed. These weak C-X...M interactions, which carbon-bound hydrogen atoms cannot emulate, can be of utmost importance in influencing the structural features of metal-halo ligand coordination chemistry.

We have been particularly interested in the versatility of metal ion coordination by fluorine- and chlorine-substituted carboxylate ligands. In alkali-metal salts of fluoro and chloro carboxylic acids, there has been ample crystallographic evidence for the existence of significant C-X...M interactions.<sup>1,2</sup> However, there has been a paucity of reported crystallographic investigations of multivalent salts/complexes of halo carboxylic acids. In these latter systems, we may anticipate that binding of "hard" metal ions would be dominated by carboxylate (oxygen) coordination, although in some instances participation of the halogen atom in metal ion binding may be of great importance.

As part of a systematic study to investigate the structural coordination chemistry of the halocarbon environments in multivalent derivatives of halo carboxylic acids, we have determined the crystal structure of calcium chloroacetate hydrate, in which the chloroacetate moiety exhibits a direct C-Cl...Ca<sup>2+</sup> mode of binding.

**Table I.** Fractional Coordinates and Equivalent Isotropic Displacement Parameters for Calcium Chloroacetate Hydrate<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> <sub>eq</sub> , Å <sup>2</sup>
Ca	0.08561 (9)	0.04037 (3)	0.75694 (8)	1.55
Cl(1)	-0.0702 (1)	0.18605 (5)	0.7497 (2)	3.98
Cl(2)	-0.3655 (2)	-0.18102 (5)	0.5818 (2)	5.50
Ow	0.3789 (4)	-0.0322 (1)	0.6986 (4)	3.00
O(1)	-0.2927 (4)	0.0635 (1)	0.7324 (3)	2.48
O(2)	-0.6030 (4)	0.0987 (1)	0.8432 (3)	2.76
O(3)	-0.0410 (4)	-0.0594 (1)	0.9017 (3)	2.18
O(4)	-0.0961 (4)	-0.0612 (1)	0.5809 (3)	2.14
C(1)	-0.4101 (5)	0.1048 (2)	0.8068 (4)	2.07
C(2)	-0.3138 (6)	0.1688 (2)	0.8668 (6)	3.33
C(3)	-0.1054 (5)	-0.0868 (1)	0.7456 (1)	1.75
C(4)	-0.1850 (7)	-0.1543 (2)	0.7687 (5)	3.13
H1(Ow)	0.378	-0.054	0.574	5.00
H2(Ow)	0.516	-0.011	0.721	5.00
H1(C2)	-0.279	0.168	1.023	5.00
H2(C2)	-0.431	0.206	0.834	5.00
H1(C4)	-0.264	-0.158	0.905	5.00
H2(C4)	-0.046	-0.186	0.774	5.00

<sup>a</sup> Estimated standard deviations in the least significant digits are given in parentheses here and in other tables.

**Table II.** Selected Bond Lengths (Å) and Angles (deg) for Calcium Chloroacetate Hydrate<sup>a</sup>

Ca-Cl(1)	3.206 (1)	C(1)-O(1)	1.254 (4)
Ca-Ow	2.418 (2)	C(1)-O(2)	1.237 (4)
Ca-O(1)	2.388 (2)	C(1)-C(2)	1.518 (5)
Ca-O(2 <sup>d</sup> )	2.331 (2)	C(2)-Cl(1)	1.778 (4)
Ca-O(3)	2.461 (2)	C(3)-O(3)	1.254 (3)
Ca-O(4)	2.665 (2)	C(3)-O(4)	1.247 (3)
Ca-O(3 <sup>b</sup> )	2.387 (2)	C(3)-C(4)	1.511 (4)
Ca-O(4 <sup>c</sup> )	2.344 (2)	C(4)-Cl(2)	1.741 (4)
O(1)-C(1)-O(2)	126.4 (3)	O(3)-Ca-O(4)	50.44 (7)
O(1)-C(1)-C(2)	119.5 (3)	O(3)-Ca-O(3 <sup>b</sup> )	72.42 (8)
O(2)-C(1)-C(2)	114.0 (3)	O(4)-Ca-O(4 <sup>c</sup> )	74.99 (8)
Cl(1)-C(2)-C(1)	112.9 (2)	Cl(1)-Ca-O(1)	60.79 (6)
O(3)-C(3)-O(4)	122.4 (3)	Cl(1)-Ca-O(2 <sup>d</sup> )	75.35 (6)
O(3)-C(3)-C(4)	115.6 (3)	Cl(1)-Ca-O(3 <sup>b</sup> )	78.75 (6)
O(4)-C(3)-C(4)	121.9 (3)	Cl(1)-Ca-O(4 <sup>c</sup> )	80.27 (6)
Cl(2)-C(4)-C(3)	115.2 (2)	Cl(1)-Ca-Ow	145.71 (7)
C(1)-Cl(1)-Ca	93.4 (1)	Cl(1)-Ca-O(3)	135.78 (6)
Ca-O(3)-Ca <sup>b</sup>	107.58 (8)	Cl(1)-Ca-O(4)	129.54 (6)
Ca-O(4)-Ca <sup>c</sup>	105.01 (8)		

<sup>a</sup> Superscripts are defined in Figure 1.

### Experimental Section

Colorless prismatic crystals of the title compound were readily grown from an aqueous solution of the salt by slow evaporation. The crystals cleave easily, are quite hygroscopic, and must be handled carefully to prevent fracturing. A well-formed single crystal of approximate dimensions 0.28 × 0.28 × 0.22 mm, which gave sharp optical extinction along three mutually perpendicular directions under crossed polarizers, was sealed in a thin-walled glass capillary tube. Unit cell constants were determined from a least-squares refinement of the setting angles of 25 reflections in the range 18° < 2θ < 37° measured with MoKα radiation on a CAD4 computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromator.

**Crystal Data:** Ca(CH<sub>2</sub>ClCOO)<sub>2</sub>(H<sub>2</sub>O), fw 245.08, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 6.186 (1) Å, *b* = 20.992 (2) Å, *c* = 6.804 (1) Å, β = 92.990 (9)°, *Z* = 4, *V* = 882.34 Å<sup>3</sup>, ρ<sub>calcd</sub> = 1.84 g/cm<sup>3</sup>, ρ<sub>measd</sub> = 1.83 g/cm<sup>3</sup>, μ(Mo Kα) = 12.6 cm<sup>-1</sup>, *T* = 292 K.

Integrated three-dimensional intensity data in quadrants *h*, *k*, ±*l* in the range 1° ≤ 2θ ≤ 53° were collected on the aforementioned diffractometer by using the ω-θ scan techniques. Absorption and secondary extinction corrections were not applied. After data reduction a total of 1670 independent reflections had *F*<sub>o</sub> ≥ 0.50σ(*F*<sub>o</sub>) and were used in subsequent calculations.<sup>5</sup>

The structure was solved by using a combination of direct and heavy-atom methods and refined by a full-matrix least-squares procedure.

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- (5) Data reduction, structure solution and refinement were carried out on IBM 4381 or VAX 8250 computers using the Enraf-Nonius SDP software package as well as other programs.<sup>6</sup>
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