on the bridge perthiolate α-sulfur gives the dimer anion and alkyl thiocyanate in a very rapid step. The dimer anion, analogous to previously established nucleophilic reactions with alkyl or sulfur halides,[27] then attacks the alkyl thiocyanate to generate the alkanethiolate-bridged dimer and thiocyanate ion. This second reaction was slow for R = Bz and extremely slow for R = Et and may in fact have been an equilibrium step for either.

The first reaction follows standard RSSR/CN^- chemistry,[40,41] while the desulfurization overall parallels production of organic sulfides from RSSR/CN^-.[42] Desulfurization is also characteristic of cyanide reactions with molybdenum sulfide and disulfide complexes, as well as some molybdenum enzymes, and thiocyanate is a common product.[2,30–33] The methaneperthiolate system $[Ir(SSMe)(Ph_2PC_2H_4PPh_2)_2]^{2+}$ has also been reported to react with cyanide.[34] In that complex, the $MeSS^-$ unit is η^2-bound, and cyanide attacks at the β-sulfur. S–S cleavage is obtained, but thiocyanate is retained as a ligand.

Crystal Structure of SMo_2*SSEt. The SMo_2*S core of the current SMo_2*SSEt is similar to the previously analyzed cores of SMo_2*SH[36] and SMo_2*SMe.[38] These contained bridging hydrosulfide and methanethiolate groups, and both also contained bridging trifluoroacetate as opposed to acetate in SMo_2*SSEt. Only some aspects of the core in SMo_2*SSEt are therefore currently addressed.

The Mo_2S_2 unit is planar; all atoms are within 0.01 Å of the least-squares plane. Disparity in Mo–S bonding within the dimer is obvious both at the bridge sulfur sites (S_b) and at dithiophosphate sulfur sites. Mo–S_b bonds are clearly longer to the tricoordinate sulfur S(2) than to S(1), the differences being 0.113 (1) Å and 0.096 (1) Å for Mo(1)–S_b and Mo(2)–S_b, respectively.

The acetate is symmetrically bridging within experimental error. Mo–O bonds are approximately 0.09 Å shorter for SMo_2*SSEt than corresponding lengths in SMo_2*SH and SMo_2*SMe which instead possessed trifluoroacetate.

The most important structural feature for SMo_2*SSEt is the clear definition of the ethaneperthiolate group. The orientation of this group shows some skew in the S(2)–S(7) bond vector away from a symmetric position relative to the Mo_2S_2 core. The displacement can be seen in Mo···S(7) distances which are 3.841 (2) Å for Mo(1) and 3.690 (2) Å for Mo(2) although Mo–S(2) distances are comparable. These distances are too long for significant, direct Mo···S(7) interaction, confirming the earlier assignment of the $EtSS^-$ ligand as bridging only by its β-sulfur.[27] Earlier structural studies on M-SSR complexes have revealed both η^1- and η^2-bonding modes for the two sulfurs of the RSS^- ligand.[16,18,22–25] The β-sulfur bridge structure has also been reported for $[(C_5H_5)_2Cr_2(NO)_2(SCMe_3)(SSCMe_3)]$.[21]

The C(25)–S(7)–S(2) linkage is quite normal[40,41] with no serious perturbation due to the β-sulfur bridging arrangement. One notable feature is the manifestation of the well-established dihedral angle for –S–S– compounds. For disubstituted organic disulfides, C–S–S–C dihedral angles tend to be 90° unless sterically precluded.[40,41,43] Present angles are 94.5 (3)° for Mo(1) and 172.0 (3)° for Mo(2) for the Mo–S(2)–S(7)–C(25) dihedral set. C(25) is thus normally posed relative to Mo(1) but trans to Mo(2). While this may indeed represent a preferred molecular geometry, fortuitous crystal packing may also be responsible.

A notable short intermolecular contact exists between S(7) atoms on one molecule and the molecule related to it by inversion but in the adjacent unit cell. The S(7)···S(7)′ distance is only 3.40 Å while the sum of van der Waals radii is 3.7 Å.[44] Interestingly, the previously addressed skew in Mo–S(2)–S(7) angles is in the direction of shortening that contact.

Acknowledgment. This work was supported by research awards from the Graduate School and from the College of Arts and Sciences of the University of Louisville and with funds from the National Science Foundation (Grant No. RII-8610671) and the Kentucky EPSCoR Program.

Registry No. **1** (R = Et), 103368-81-6; **1** (R = Bz), 103368-82-7; **2** (R = Bz), 103383-36-4; SMo_2*S^-, 112482-65-2; BzSCN, 3012-37-1; EtSCN, 542-90-5; BzSSH, 3492-66-8; EtSSH, 74004-30-1; CN^-, 57-12-5.

Supplementary Material Available: Calculated hydrogen positions (Table V), displacement parameters (Table VI), bond lengths (Table VII) and angles (Table VIII) excluded from main text, Mo(1)–Mo(2)–S(1)–S(2) least-squares plane (Table IX), and unit cell diagram (Figure 2) (9 pages); a table of calculated and observed structure factors (53 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47905

Synthesis and Structure of Niobium(V) and Tantalum(V) Organoimido Compounds Containing 2,6-Diphenylphenoxide Ligation

Robert W. Chesnut, Phillip E. Fanwick, and Ian P. Rothwell*[1]

Received July 16, 1987

There is currently considerable research interest in the inorganic and organometallic chemistry associated with 2,6-dialkylphenoxide[2,3] and thiophenoxide[4,5] ligation. Our group has been particularly interested in the use of the sterically bulky 2,6-di-*tert*-butylphenoxide group as an ancillary ligand attached to early transition-metal centers.[6] However, the ligand itself has been found, under somtimes mild conditions, to undergo cyclometalation reactions to form six-membered metallacycle rings derived by activation of one of the carbon–hydrogen bonds of a *tert*-butyl

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Table I. Positional Parameters and Their Estimated Standard Deviations for **1a**

atom	x	y	z	B,[a] Å^2
Nb	−0.02210 (5)	0.01984 (3)	0.21390 (2)	2.777 (8)
O(10)	−0.0661 (4)	−0.0311 (2)	0.1406 (2)	3.80 (9)
O(20)	0.1327 (4)	0.0529 (2)	0.2499 (2)	3.50 (9)
O(30)	−0.0676 (4)	0.1094 (2)	0.1792 (2)	3.66 (9)
N(40)	−0.1322 (5)	0.0060 (2)	0.2695 (2)	3.6 (1)
N(50)	0.0676 (5)	−0.0837 (3)	0.2429 (3)	4.3 (1)
C(11)	−0.1096 (6)	−0.0849 (3)	0.1079 (3)	3.7 (1)
C(12)	−0.0313 (7)	−0.1783 (4)	0.0686 (3)	4.2 (1)
C(13)	−0.0780 (8)	−0.1783 (4)	0.0391 (3)	5.7 (2)
C(14)	−0.1942 (8)	−0.2006 (4)	0.0468 (4)	6.2 (2)
C(15)	−0.2727 (7)	−0.1652 (4)	0.0861 (4)	5.7 (2)
C(16)	−0.2346 (7)	−0.1071 (3)	0.1173 (3)	3.6 (1)
C(21)	0.2161 (5)	0.0813 (3)	0.2876 (3)	3.2 (1)
C(22)	0.2817 (5)	0.1398 (3)	0.2675 (3)	5.3 (2)
C(23)	0.3650 (7)	0.1693 (4)	0.3077 (3)	5.3 (2)
C(24)	0.3853 (7)	0.1439 (4)	0.3654 (4)	6.1 (2)
C(25)	0.3244 (7)	0.0860 (4)	0.3839 (3)	3.7 (1)
C(26)	0.2385 (6)	0.0541 (3)	0.3463 (3)	3.7 (1)
C(31)	−0.1682 (6)	0.1803 (3)	0.2251 (3)	4.5 (2)
C(32)	−0.2252 (6)	0.1803 (3)	0.2251 (3)	4.5 (2)
C(33)	−0.3341 (6)	0.2180 (3)	0.2137 (4)	5.6 (2)
C(34)	−0.3870 (7)	0.2244 (4)	0.1595 (5)	6.7 (2)
C(35)	−0.3299 (7)	0.1967 (4)	0.1080 (4)	6.1 (2)
C(36)	−0.2174 (6)	0.1599 (3)	0.1152 (3)	4.6 (2)
C(41)	−0.2237 (9)	−0.0083 (5)	0.3148 (4)	7.6 (2)
C(51)	0.1885 (8)	−0.1000 (4)	0.2165 (4)	6.7 (2)
C(52)	−0.012 (1)	−0.1436 (3)	0.0510 (3)	6.9 (2)
C(121)	0.1014 (7)	−0.1011 (3)	0.0610 (3)	4.5 (2)
C(122)	0.1390 (8)	−0.0333 (4)	0.0524 (3)	5.7 (2)
C(123)	0.02660 (9)	−0.0707 (5)	0.0487 (5)	8.1 (2)
C(124)	0.3519 (9)	−0.0707 (5)	0.0487 (5)	9.4 (3)
C(125)	0.3140 (9)	−0.1359 (5)	0.0567 (5)	8.2 (3)
C(126)	0.1905 (8)	−0.1522 (4)	0.0626 (4)	6.2 (2)
C(161)	−0.3222 (6)	−0.0727 (3)	0.1559 (4)	4.5 (2)
C(162)	−0.3425 (6)	−0.0028 (3)	0.1559 (4)	4.9 (2)
C(163)	−0.4316 (7)	0.0268 (4)	0.1944 (5)	7.4 (2)
C(164)	−0.3995 (7)	−0.0119 (5)	0.2328 (5)	8.9 (3)
C(165)	−0.4813 (8)	−0.0814 (5)	0.2344 (5)	9.3 (3)
C(166)	−0.3942 (7)	−0.1111 (4)	0.1988 (4)	6.6 (2)
C(221)	0.2684 (5)	0.1701 (3)	0.2056 (3)	3.7 (1)
C(222)	0.2880 (7)	0.1329 (3)	0.1534 (3)	4.5 (2)
C(223)	0.2909 (8)	0.1653 (4)	0.0975 (4)	6.0 (2)
C(224)	0.2716 (8)	0.2360 (4)	0.0917 (4)	5.9 (2)
C(225)	0.2492 (8)	0.2722 (4)	0.1427 (4)	6.3 (2)
C(226)	0.2469 (7)	0.2408 (3)	0.2012 (4)	5.3 (2)
C(261)	0.1768 (6)	−0.0091 (4)	0.3696 (3)	4.0 (1)
C(262)	0.0577 (7)	−0.0080 (4)	0.3930 (4)	5.9 (2)
C(263)	0.0077 (9)	−0.0664 (5)	0.4171 (4)	7.6 (2)
C(264)	0.070 (1)	−0.1259 (4)	0.4180 (4)	7.9 (2)
C(265)	0.1856 (9)	−0.1290 (4)	0.3941 (4)	7.4 (2)
C(266)	0.2385 (7)	−0.0700 (4)	0.3704 (4)	4.8 (2)
C(321)	−0.1767 (6)	0.1739 (3)	0.2870 (4)	4.8 (2)
C(323)	−0.0068 (8)	0.1799 (4)	0.3596 (3)	6.1 (2)
C(324)	−0.090 (1)	0.1653 (5)	0.4064 (4)	8.1 (3)
C(325)	−0.2137 (9)	0.1550 (5)	0.3946 (4)	6.3 (2)
C(326)	−0.2527 (8)	0.1603 (4)	0.3366 (4)	6.3 (2)
C(361)	−0.1574 (7)	0.1332 (4)	0.0597 (3)	5.6 (2)
C(362)	−0.0362 (8)	0.1524 (4)	0.0453 (4)	6.5 (2)
C(363)	0.0178 (9)	0.1307 (6)	−0.0079 (4)	9.0 (3)
C(364)	−0.044 (1)	0.0901 (7)	−0.0468 (4)	11.1 (3)
C(365)	−0.160 (1)	0.0696 (7)	−0.0335 (4)	10.4 (4)
C(366)	−0.2163 (8)	0.0909 (6)	0.0194 (4)	7.4 (2)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Nb(OAr\text{-}2,6\text{-}Ph_2)_3(NMe)(HNMe_2)$ (**1a**)

Nb–O(10)	1.940 (4)	O(20)–C(21)	1.340 (7)
Nb–O(20)	1.958 (4)	O(30)–C(31)	1.353 (9)
Nb–O(30)	1.965 (5)	N(40)–C(41)	142 (1)
Nb–N(40)	1.720 (5)	N(50)–C(51)	1.46 (1)
Nb–N(50)	2.326 (6)	N(50)–C(52)	1.45 (1)
O(10)–C(11)	1.354 (8)		
O(10)–Nb–O(20)	135.1 (2)	O(30)–Nb–N(50)	168.4 (2)
O(10)–Nb–O(30)	94.4 (2)	N(40)–Nb–N(50)	87.8 (3)
O(10)–Nb–N(40)	109.3 (2)	Nb–O(10)–C(11)	156.3 (4)
O(10)–Nb–N(50)	83.2 (2)	Nb–O(20)–C(21)	163.2 (4)
O(20)–Nb–O(30)	94.3 (2)	Nb–O(30)–C(31)	139.3 (4)
O(20)–Nb–N(40)	111.2 (2)	Nb–O(40)–C(41)	177.6 (6)
O(20)–Nb–N(50)	79.7 (2)	Nb–N(50)–C(51)	117.0 (5)
O(30)–Nb–N(40)	103.7 (2)	Nb–N(50)–C(52)	117.2 (5)

group.[7] Following these studies we have turned our attention to the ligand 2,6-diphenylphenoxide ($OAr\text{-}2,6\text{-}Ph_2$)[9,10] a group that offers the possibility for related metallacycle formation, only this time via activation of an aromatic carbon–hydrogen bond. The thermolysis of mixed alkyl and aryloxides of niobium and tantalum containing this ligand does indeed lead to metallacycle formation and alkane elimination.[11] However, we have also found that for molybdenum it is possible to carry out cyclometalation chemistry using an amido leaving group (eq 1).[12]

$$Mo(NMe_2)_4 + 3HOAr\text{-}2,6\text{-}Ph_2 \rightarrow Mo(OC_6H_3PhC_6H_4)(OAr\text{-}2,6\text{-}Ph_2)_2(HNMe_2) + 3HNMe_2 \quad (1)$$

This has led us to investigate the chemistry of group 5 metal–amido compounds containing 2,6-diphenylphenoxide coligation. Although in this case no metallacycle formation is observed, we do find the high-yield formation of a metal–imido functional group.[13] This note reports the synthesis and structure of these new compounds.

Results and Discussion

The addition of 2,6-diphenylphenol ($HOAr\text{-}2,6\text{-}Ph_2$; 3 equiv) to a toluene solution of the pentaamide compounds $M(NMe_2)_5$[14] results in the rapid evolution of dimethylamine. Warming the mixture to 115 °C for 3 h followed by slow cooling results in the formation of the imido compounds $M(OAr\text{-}2,6\text{-}Ph_2)_3(NMe)(HNMe_2)$ (M = Nb (**1a**), Ta (**1b**)) as large colorless or yellow blocks, respectively. In the ^1H NMR spectra of sparingly soluble **1**, the *N*-methylimido group appears as a sharp singlet at δ 1.94 (Nb) or 1.49 (Ta). These values are significantly upfield of the position one might expect, given the demonstrated tendency of early transition-metal M=NR functional groups to shift hydrogens attached to the α-carbon downfield. However, the presence of 2,6-diphenylphenoxide ligands in the coordination sphere has been shown to lead to a dramatic upfield shifting of the resonances of adjacent ligands due to the orientation of the phenyl substituents attached to the aryloxide ring.[9] This effect also presumably explains the even further upfield position of the methyl groups of the coordination dimethylamine ligand. Solid-state I.R. studies clearly show the $\bar{\nu}$(NH) of the $HNMe_2$ ligand. The strong bands observed at 1240 (**1a**) and 1234 cm^{-1} (**1b**) may tentatively be assigned to the metal–imido stretch, although the presence of numerous bands in the 1000–1300-cm^{-1} region make a conclusive assignment impossible.

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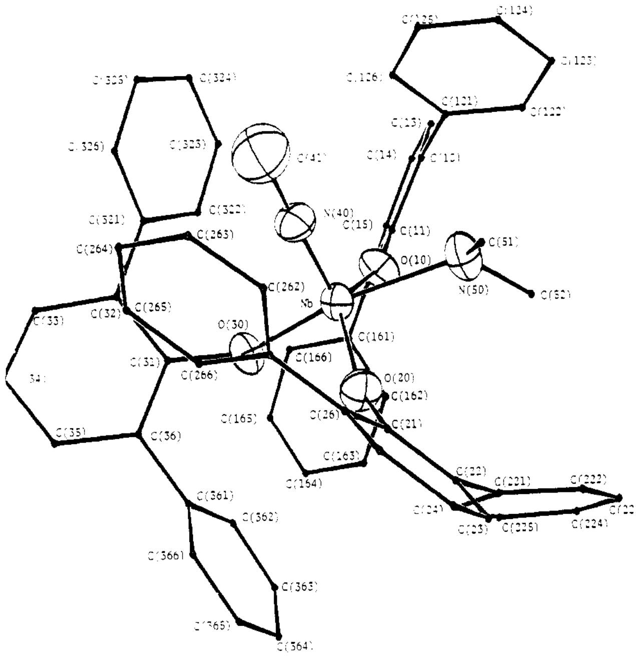

Figure 1. ORTEP view of $Nb(OAr\text{-}2,6\text{-}Ph_2)_3(NMe)(HNMe_2)$ (**1a**) emphasizing the central coordination sphere.

A single-crystal X-ray diffraction study of the niobium compound (**1a**) was carried out. An ORTEP view and labeling scheme is shown in Figure 1 while Tables I and II contain fractional coordinates and some selected bond distances and angles. The geometry about niobium can best be described as distorted trigonal bipyramidal with an equational amido group. The considerable distortions from this geometry probably reflect the steric noninnocence of the $OAr\text{-}2,6\text{-}Ph_2$ ligand compared to the NMe and $HNMe_2$ groups. The Nb–N(40) distance of only 1.720 (5) Å is comparable to distances reported for other niobium(V)- and tantalum(V)-imido compounds.[13,15,16] This contrasts with the much longer distance, 2.326 (6) Å, to the simple dimethylamine ligand. This difference of ~0.6 Å compares well with differences in these two types of bond reported elsewhere.[17] The Nb–O distances of 1.94–1.97 Å fall in the range typical for aryloxides bound to Nb(V), while the moderately large Nb–O–Ar angles are not unexpected.[6,9]

The pathway whereby the methylimido ligands in (**1**) are formed from dimethylamido groups is uncertain. The dealkylation of NEt_2 ligands to generate an ethylimido function at tantalum has been shown to proceed by initial cyclometalation at the α-carbon to generate an η^2-*N*-ethyleneamine (EtNCHMe) intermediate.[18,19] Loss of ethylene then takes place to complete the transformation.[19] Although an analogous cyclometalation of NMe_2 at Ta(V) has been documented,[20] it is difficult to envisage a ready pathway to generate the methylimido function. Analysis of the volatiles from the reaction indicated the presence of only dimethylamine. No measurable amounts of trimethylamine (NMe_3) were detected by either ^1H NMR or GC/MS analysis.

Table III. Crystal Structure Determination for **1a**

formula	$NbO_3N_2C_{57}H_{49}$
fw	902.94
space group	$P2_12_12_1$
a, Å	10.808 (2)
b, Å	19.499 (4)
c, Å	21.801 (3)
α, deg	90
β, deg	90
γ, deg	90
Z	4
V, Å^3	4594 (2)
d(calcd), g/cm^3	1.305
cryst size	0.70 × 0.60 × 0.47
cryst color	yellow
radiation	Mo Kα (λ = 0.71073 Å)
linear abs coeff, cm^{-1}	2.95
temp, °C	22
detector aperture, mm	(1.5 + tan θ) wide; 4.0 high
takeoff angle, deg	4.90
scan speed, deg/min	variable
scan width, deg	0.8 + 0.35 tan θ
bkgd counts, s	50% of scan time
2θ range, deg	4–45
no. of unique data	3414
no. of unique data with $I_0 > 3.00\sigma$	2641
R(*F*)	0.034
$R_w(F)$	0.043
goodness of fit	0.959

Experimental Section

Synthesis of $Nb(OAr\text{-}2,6\text{-}Ph_2)_3(NMe)(HNMe_2)$ (1a). Addition of 2,6-diphenylphenol ($HOAr\text{-}2,6\text{-}Ph_2$,m 1.73 g 7.0 mmol) to a solution of $Nb(NMe_2)_5$ (0.70 g, 2.2 mmol) in toluene (30 cm^3) resulted in the initial evolution of $HNMe_2$. The mixture was warmed (115 °C) for 3 h before being cooled slowly. Large blocks of the product were formed, and these were filtered, washed with hexane, and dried. Yield = 1.10 g (55%). More product could be obtained on concentrating the mother liquor. Anal. Calcd for $NbC_{57}H_{49}O_3N_2$: C, 75.82; H, 5.47; N, 3.10. Found: C, 75.61; H, 5.59; N, 2.87. ^1H NMR ($C_6D_5CD_3$, 30 °C): δ 1.94 (s, Nb=NC*H*$_3$), 1.08 (broad, NbHN*Me*$_2$), 6.9–7.2 (m, aromatics). IR (Nujol mull): 3269 (w), 1596 (m), 1577 (w), 1405 (s), 1306 (w), 1278 (m), 1240 (s), 1180 (w), 1153 (w), 1082 (m), 1069 (m), 960 (w), 907 (w), 877 (s), 756 (s), 702 (s), 624 (s), 612 (m) cm^{-1}.

$Ta(OAr\text{-}2,6\text{-}Ph_2)_3(NMe)(HNMe_2)$ (1b). A procedure identical with that above but using $Ta(NMe_2)_5$ (0.43 g, 1.1 mmol) and $HOAr\text{-}2,6\text{-}Ph_2$ (0.83 g, 3.4 mmol) yielded 0.56 g (53%) of compound **1b**, again as large blocks. Anal. Calcd for $TaC_{57}H_{49}O_3N_2$: C, 69.09; H, 4.98; N, 2.83. Found: C, 68.60; H, 4.86; N, 1.77. Compound **1b** consistently gave low nitrogen analyses. ^1H NMR ($C_6D_5CD_3$, 30 °C): δ 1.49 (s, TaNC*H*$_3$), 0.94 (broad, TaHN*Me*$_2$), 6.9–7.2 (m, aromatics). IR (Nujol mull): 3249 (w), 1596 (w), 1578 (w), 1493 (w), 1407 (s), 1308 (w), 1277 (w), 1234 (s), 1179 (w), 1155 (w), 1080 (w), 1070 (m), 954 (m), 890 (s), 871 (s), 755 (s), 703 (s), 630 (m), 610 (w) cm^{-1}.

Crystallographic Studies. Details of the data collection procedures and structure refinement methods have been given previously.[9a] Table III contains pertinent crystallographic data. The crystals were examined under deoxygenated Nujol and mounted in an appropriate sized capillary with epoxy resin. The hydrogen atom positions were calculated after several cycles of anisotropic refinement, assuming idealized geometries and a bond distance of 0.95 Å. No correction for extinction was performed. The enantiomorph shown was chosen on the basis of *R* values: *R* = 0.0355; R_w = 0.0453; goodness of fit = 1.010 for the other enantiomer.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8612063 to I.P.R.) for support of this research. I.P.R. also gratefully acknowledges the Camille and Henry Dreyfus Foundation for the award of a Teacher-Scholar Grant and the Alfred P. Sloan Foundation for the award of a fellowship.

Registry No. **1a**, 112347-59-8; **1b**, 112347-60-1; $Nb(NMe_2)_5$, 19824-58-9; $Ta(NMe_2)_5$, 19824-59-0; Me_2NH, 124-40-3.

Supplementary Material Available: Tables of anisotropic temperature factors, hydrogen atom parameters, full bond distances and angles, and torsional angles (10 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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