Volume 12
Number 9
September 1973

Inorganic Chemistry

Contribution No. 2000 from the Central Research Department, Experimental
Station, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898

Stereochemical Lability of Eight-Coordinate Complexes

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Received May 7, 1973

Ligand inequivalence and evidence for stereoisomers in eight-coordinate complexes (solution state) have been probed by low-temperature ^{1}H and ^{13}C nmr spectra. The $Mo(CN)_8{}^{4-}$ and $W(CN)_8{}^{4-}$ ions appear to be nonrigid down to −160° (^{13}C). However, there are anomalous features in the electronic spectrum of $[(n\text{-}C_3H_7)_4N]_4W(CN)_8$ which suggest this salt may have a nondodecahedral geometry for the $W(CN)_8{}^{4-}$ complex. Symmetrical and unsymmetrical dithiocarbamato complexes of Ti, Zr, and Nb(IV) appear to be nonrigid down to −100 to −160°. However, there is evidence that the carbon atoms (^{13}C) and hydrogen (^{1}H) atoms are not very sensitive probes of environmental inequivalence for the dithiocarbamate alkyl substituents, especially with respect to possible stereoisomers derived from unsymmetrically substituted chelate ligands.

Introduction

Eight-coordination is a stereochemical class with three structural (polytopal) forms that not only are very similar with respect to total energy[1-6] but also are closely related to each other by small relative displacements of ligating atoms.[1,2,4,5,7,8] Stylized rearrangements that interconvert the three are shown in Figure 1; each step requires primarily stretching (or compression) of one or two polyhedral edges (or diamond[7] face) to generate a square face. A stretching of one and two b edges in the dodecahedron yields the C_{2v} bicapped trigonal prism and D_{4d} antiprism, respectively; and a concerted stretching of two b edges can generate a new dodecahedron with A and B sites permuted in a single step. The latter is the Hoard–Silverton rearrangement[1] (Figure 2), an idealized rearrangement mode that may well largely account for the relatively pervasive stereochemical nonrigidity in this structural class. In fact, the only class of compounds for which limiting slow-exchange nmr spectra have been observed in this coordination group has a dodecahedral geometry whose spin Hamiltonian is unaffected by the Hoard–Silverton rearrangement.[9-11] This class comprises metal tetrahydrides of the type $H_4M(PR_3)_4$ which have dodecahedral form with phosphine ligands at B sites.

Low-temperature nmr data, described herein, establish maximal barriers to intramolecular rearrangements for two model coordination forms (1) $M(CN)_8{}^{4-}$ and (2) $M(chel)_4$. Also described are the relationships between intramolecular rearrangements for coordination compounds and for clusters in the eight-atom family.

Results and Discussion

Octacyanometalate Ions. The $Mo(CN)_8{}^{4-}$ anion in crystalline $K_4Mo(CN)_8 \cdot 2H_2O$ is a dodecahedron.[12,13] Detailed Raman studies[14] establish that dodecahedral form, not an alternative such as the square antiprism, is the geometry for the anion on dissolution of the salt in water and that dodecahedral form also prevails for $W(CN)_8{}^{4-}$ in solutions of $K_4W(CN)_8 \cdot 2H_2O$ in water. Earlier this author[8] had reported a single ^{13}C resonance for $K_4Mo(CN)_8 \cdot 2H_2O$ (^{13}C enriched) in H_2O. This result has been confirmed with $K_4Mo(CN)_8 \cdot 2H_2O$ in water and water–methanol to nearly 0°; under these same conditions the analogous tungsten salt gave a single ^{13}C cyanide resonance. These data indicate a relatively low barrier to a Hoard–Silverton rearrangement (or any other physical process that would permute A and B sites in the dodecahedron). (See Figures 1 and 2.) Rearrangement barriers in ML_5 five-coordinate complexes are 7-8 kcal/mol or less.[4,15,16] The barrier to the Hoard–Silverton process (Figure 2) in ML_8 species should be comparable. Hence low-temperature nmr studies of the $M(CN)_8{}^{4-}$ ions are necessary to probe for limiting slow-exchange spectra.

To explore the ^{13}C nmr spectra of octacyanomolybdate ions at low temperatures, salts soluble in $CHClF_2$-CH_2Cl_2 (90:10), an excellent low-temperature medium of low

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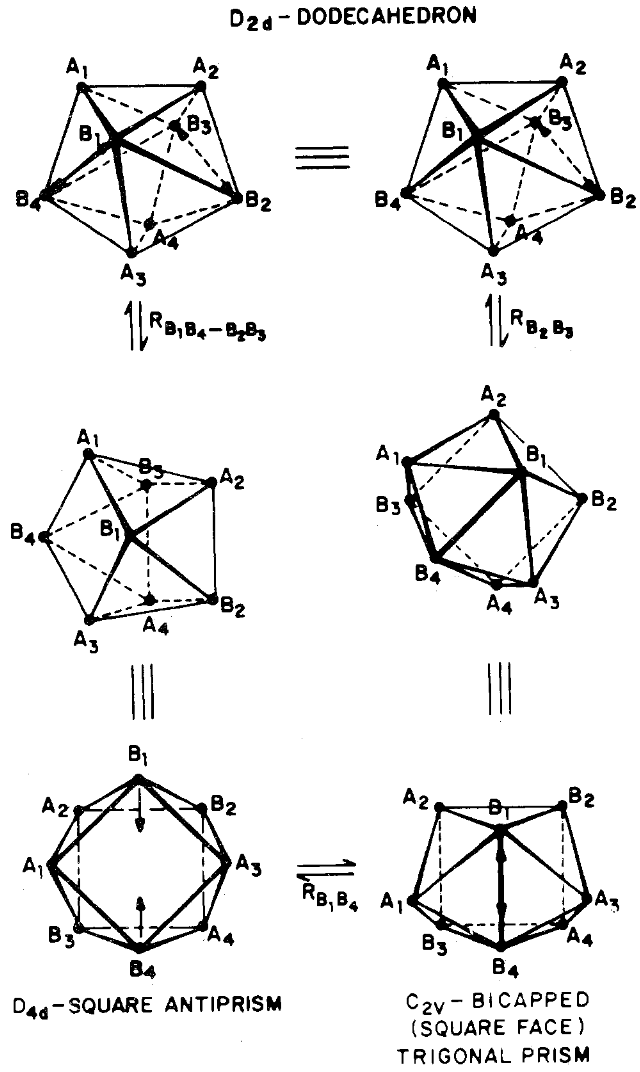

Figure 1. A stylized representation of the close interrelationships of three idealized eight-coordinate geometries. The dodecahedron on the left is converted to the square antiprism below by stretching of b edges. The square antiprism is then converted, as shown on the bottom line, by a minor edge compression to the C_{2v} bicapped trigonal prism on the lower right. This latter form can also be directly generated from the dodecahedron by stretching of a single b edge as shown in the right-hand column.

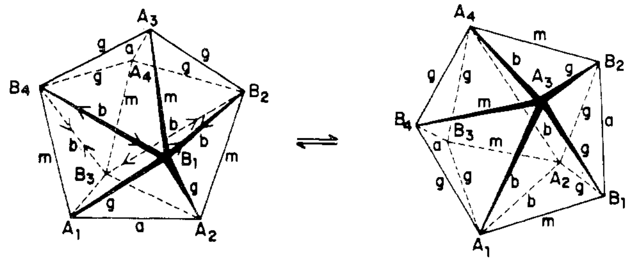

Figure 2. Hoard–Silverton[1] concerted rearrangement in which A and B sites are permuted by elongation and compression of complementary b edges in the dodecahedron.

viscosity, were sought. The tetra-*n*-propylammonium salts met all requirements. The analogous tetra-*n*-butylammonium salts were significantly less soluble in the $CHClF_2$-CH_2Cl_2 mixture; an X-ray analysis of the $[(n\text{-}C_4H_9)_4N]_4Mo(CN)_8$ salt has shown that the $Mo(CN)_8^{4-}$ ion in this salt is essentially dodecahedral (actual D_2 symmetry).[17] The cyanide ^{13}C nmr spectra of the propylammonium salts of $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ and the butylammonium salt of $Mo(CN)_8^{4-}$ consisted of single ^{13}C cyanide resonances down to temperatures of ~−140 to −165°. The same result was obtained for water-ethanol-hexafluoroacetone solutions down to about −50°.

If it is assumed that dodecahedral geometry is retained in the highly nonpolar $CHClF_2$-CH_2Cl_2 medium, the nmr results point to a very low barrier to internal rearrangements. The electronic spectrum and the infrared CN stretching region of $[(n\text{-}C_3H_7)_4N]_4Mo(CN)_8$ are essentially the same in H_2O and in CH_2Cl_2 and are very similar to $K_4Mo(CN)_8 \cdot 2H_2O$ in water. Hence the essential structural features are probably retained. This is not true for $[(n\text{-}C_3H_7)_4N]_4W(CN)_8$. For this salt, the electronic spectrum is the same in H_2O and in CH_2Cl_2 but drastically different from that of $K_4W(CN)_8 \cdot 2H_2O$. Hence, in the tungsten case there appears to be the possibility of structural change. (Reconversion of the butyl to the potassium salt is quantitative.) This possible effect of cation on the polytopal form is the subject of another study that will be reported shortly.[18]

Ion pairing or clustering should be extensive for $[(n\text{-}C_3H_7)_4N]_4Mo(CN)_8$ in the $CHClF_2$-CH_2Cl_2 medium. If there is a stereochemical facet to this ordering with cations centering on opposite b edges of the dodecahedron, there may be some stabilization of a square-face polytopal form. This could be manifest in either one of two ways. The interaction may simply lower the barrier to the Hoard-Silverton rearrangement by lowering the energy level of the intermediate or transitional square-antiprismatic state. Alternatively, the stabilization may be sufficiently large so as to render the square-antiprismatic geometry the ground-state form. With associated cations, this would be a quasi ten-coordinate complex of symmetrically bicapped square-antiprismatic form. The filled d_{z^2} orbital for such d^2 complexes lies along the $\bar{8}$ axis and could interact with positively charged species. However, the tetra-*n*-propylammonium cation has a quite bushy hydrocarbon periphery and is rather unlikely to interact in such a stereospecific fashion. There are no supportive data for substantive anion or cation effects on polytopal rearrangements in coordination compounds; a specific set well examined in this context is the $M(PR_3)_5$ cations and no detectable anion effect has been discerned.[15] On the other hand, substantial solvent effects on rearrangement rates have been reported[19] in polyhedral boranes ($B_{10}CH_{11}^-$). Here a cation involvement or an ion-clustering effect upon geometry in these framework rearrangements is a distinct possibility. It is proposed that rearrangements and even changes in ground-state geometry may be discernible in studies of polyhedral boranes. An especially attractive model for study is $B_8H_8^{2-}$ (or $B_{11}H_{11}^{2-}$)[20] where there is preliminary evidence[20c] that the character of the anion and the polarity and basicity of the solvent effect structural changes in the cluster ion. This polyhedral borane area is under study[20c] as a complement to comprehensive spectral (electronic, vibrational, and nmr) investigations and X-ray studies of the octacyanometalate ions in which the associated cations are varied

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extensively in charge (charge density), symmetry, and hydrophilic character.

Chelate Structures. In eight-coordinate chelate structures, polytopal and stereochemical forms may be stabilized by matching of certain edges of the polyhedron to the bite (separation of ligating atoms) of relatively rigid chelate ligands. Short bites referenced to optimal metal-ligating atom bond distances generally lead to the dodecahedral form with the chelate ligands spanning m edges–D_{2d} (*mmmm*) stereoisomers[21] (see Figure 2). The dithiocarbamate ligand meets such qualifications and has additional attractive features. Unsymmetrical alkyl group substitution may be employed as a further probe of stereochemistry and appropriate alkyl groups can confer on the chelate complexes the requisite high solubility in nonpolar solvents for low-temperature nmr studies. Finally, it has been demonstrated that *N*-alkyl substituents can serve to monitor geometry and stereochemistry: $[(CH_3)_2NCS_2]_3Mo(NO)$ which has nearly pentagonal-bipyramidal geometry with an axial NO group shows the four-line *N*-CH_3 proton resonance required for this structure and stereochemistry.[22] Accordingly, chelates of the type first described by Bradley and coworkers[23] were prepared and the low-temperature ^{13}C and ^1H nmr spectra were explored. All these should have the dodecahedral D_{2d} (*mmmm* isomer[1]) form as established[24] for $Ti[S_2CN(C_2H_5)_2]_4$. Thus there should be two sets of alkyl environments in symmetrically substituted dithiocarbamato complexes and more than two if the nitrogen atom has two different alkyl substituents.

Spectroscopic equivalence of *N*-alkyl groups was found in $M[S_2CN(C_2H_5)_2]_4$ and $M[S_2CN(CH_2CH_2CH_3)_2]_4$ with M = Ti, Zr, and Nb(IV) to temperatures in the range of −50 to ∼−140°. Solvents employed were CS_2-CD_2Cl_2 and $CHClF_2$-CD_2Cl_2 (80:20). This characterization is based on ^1H nmr studies to temperatures of −110° (100 MHz), −160° (90 MHz), and −50° (220 MHz) and ^{13}C nmr studies to −140° (22.63 MHz). In all cases the proton spectra began to broaden at ∼+5°. Broadening was simply progressive with further temperature decrease; fine structure was obscured at the low-temperature limits (−100 to −160°). Broadening is ascribed to lower rates of molecular tumbling with the concomitant adverse effect upon the relaxation times. This phenomenon is not unexpected for these large molecules with projecting alkyl groups.

Equivalence could have its origin in at least three phenomena. One is accidental degeneracy in chemical shifts, an unlikely explanation in view of the number of derivatives examined and the two different nuclei, ^1H and ^{13}C, used as probes. Rapid polytopal isomerization is a plausible alternative; the Hoard–Silverton rearrangement suffices, in one step, to remove the alkyl group inequivalence in these dithiocarbamate complexes (Figure 2). The third alternative is an "arm off" dissociation of a chelate ligand to give a seven-coordinate reaction intermediate which must then intramolecularly rearrange to effect ligand equivalence.[25] The experimental data provide no basis for distinctions between the last two alternatives but the first of these two, for pure simplicity, seems the more likely explanation. This explanation would apply also to analogous studies of other eight-coordinate complexes,[26-28] although very low temperatures were not explored in these studies.

Unsymmetrically substituted dithiocarbamatometal complexes were also examined, specifically the *N*-methyl,*N*-*n*-propyl derivative of zirconium. For this complex, down to −100°, there was a single methyl and a single *n*-propyl proton resonance composed of triplet methyl, multiplet methylene (^{b}C), and complex triplet methylene (^{c}C) sets. The ^{13}C spectrum composed of two methyl and two methylene resonances did not change down to −140°. Single *N*-methyl and single *N*-propyl resonances can be achieved in a rigid dodecahedral complex with *mmmm* ligand attachment in either one of two stereoisomers (propyl groups over either A or B sites). However, precision models show no steric feature that would favor any stereospecific disposition of *N*-alkyl groups. There are six possible stereoisomers in the *mmmm* dodecahedral form with unsymmetrical ligands. All these should be present in solution. The absence of any indication of stereoisomers suggests that there is some dynamic process to account for ligand equivalence. A concerted Hoard–Silverton rearrangement cannot alone account for this result unless methyl and propyl resonance positions (^1H and ^{13}C) are insensibly affected by the character of nearest neighbor *N*-alkyl groups and are only distinguished in a slow-exchange limit (not yet detected) by A and B site environments. If square-antiprismatic form is a reaction intermediate of reasonable lifetime, it is possible to rationalize ligand equivalence in a many-step process.[4,8,29] Nevertheless it is surprising that a multistep process, necessarily traversing stereoisomers of higher energy, would have so low a net activation energy. A similar rationale would appear necessary to account for nmr results for chelates like $Zr(CF_3COCHCOCH_3)_4$,[26] although the ground-state polytopal form is probably square antiprismatic.

The data for the aforementioned seven-coordinate dithiocarbamatomolybdenum complex[22] would strongly suggest that the *N*-alkyl groups may serve as stereochemical sensors. However, a final result for the eight-coordinate complexes raises a disquieting point. A mixture of chelate complexes was prepared consisting of $Zr[S_2CN(C_2H_5)_2]_x[S_2CN(n\text{-}C_3H_7)_2]_{4-x}$ with *x* primarily 1, 2, and 3. The solution ^1H nmr showed only single CH_3 and CH_2 (*N*-C_2H_5) multiplets and single CH_3, CH_2, and CH_2 (*N*-C_3H_7) multiplets. In essence, the spectrum was identical with a composite of those for the pure diethyl and pure dipropyl derivatives. No significant proton nmr line shape changes were evident to −160° except for the progressive broadening with temperature decrease analogous to those observed for all other dithiocarbamato complexes reported here. Perhaps the *N*-alkyl group resonances are sensitive only to A and B site environments in the dodecahedron and are not detectably affected by what are minor changes in the relatively distant *N*-alkyl groups. A test of this possibility is being sought through synthesis of dithiocarbamatometal complexes with *N*-alkyl and *N*-perfluoroalkyl substituents.

Experimental Section

Preparation of Compounds. The dithiocarbamatometal com-

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[25] Intermolecular exchange of ligands in these complexes is not rapid. There was no nmr evidence of fast exchange in the $Ti[S_2CN(n\text{-}C_3H_7)_2]_4$–$Zr[S_2CN(n\text{-}C_3H_7)_2]_4$ system at 80°. Also synthesis of mixed-chelate complexes by heating the $Zr[S_2CNR_2]_4$–$Zr[S_2CNR'_2]_2$ mixture was unsuccessful.

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Table I. Nmr Parameters (22°)[a] For Eight-Coordinate Complexes[b]

Complex	Nucleus	a′	δ_a (*J*)	δ_b (*J*)	δ_c (*J*)	δ_d
$Zr[S_2CN(^cCH_2{}^aCH_3)_2]_4$	^1H		1.21 (7.0)		3.77 (7.0)	
$Zr[S_2C^dN(^cCH_2{}^bCH_2{}^aCH_3)_2]_4$	^1H		0.88 (7.5)	1.65 (7.0)	3.66 (7.0)	
	^{13}C[a]		−140.7	−171.7	−180.9	+10.6
$Zr[S_2CN(^{a'}CH_3)(^cCH_2{}^bCH_2{}^aCH_3)]_4$	^1H	2.84	0.66 (7.2)	1.37 (7.0)	3.38 (7.0)	
$Ti[S_2C^dN(^cCH_2{}^bCH_2{}^aCH_3)_2]_4$	^1H		0.88 (7.5)	1.65 (~7.1)	3.63 (~7.1)	
	^{13}C[a]		−107.0	−139.1	−148.5	−10.7
$Nb[S_2CN(^cCH_2{}^bCH_2{}^aCH_3)_2]_4$	^1H		0.94 (7.3)	1.73[c]	3.68[c]	
$Mo(CN)_8{}^{4-}$	^{13}C[d]		−42.7			
$W(CN)_8{}^{4-}$	^{13}C[d]		−37.7			

[a] ^{13}C spectra at −75°; carbon disulfide–dichloromethane solution. [b] δ values in ppm (positive values to higher frequency than reference) with $(CH_3)_4Si$ and CS_2 as zero references in ^1H and ^{13}C spectra, respectively. *J* values in Hz. Values are approximate for carbon atoms b and c in the propyl derivatives. [c] Broad resonances. [d] ^{13}C chemical shifts for $CHClF_2$–CD_2Cl_2 (80:20) solutions of the tetra-*n*-propylammonium salts at ~−100°.

plexes were prepared according to the literature procedures of Bradley and coworkers[23] and were purified by recrystallization. Sample analytical data are for $M[S_2CN(n\text{-}C_3H_7)_2]_4$. *Anal.* Calcd for the Ti complex: C, 44.7; H, 7.5. Found: C, 44.7; H, 7.6. Calcd for the Zr complex: C, 42.2; H, 7.1. Found: C, 42.3; H, 7.2. Nmr solvents included dichloromethane–toluene, carbon disulfide, carbon disulfide–dichloromethane, and difluorochloromethane–fluorodichloromethane.

The mixed $(C_2H_5)_2NCS_2{}^-$ and $(n\text{-}C_3H_7)_2NCS_2{}^-$ derivatives of zirconium were prepared by adding $ZrCl_4$ to a solution containing equivalent amounts of the lithium salts of diethylamine and di-*n*-propylamine. The mixed-amino derivatives were vacuum distilled and treated with carbon disulfide.[23] Vacuum distillation gave little evidence for the presence of either $Zr[S_2CN(C_2H_5)_2]_4$ or $Zr[S_2CN(n\text{-}C_3H_7)_2]_4$; significant fractions were collected at 144, 144–149, and 152–153° (0.001 mm) and were combined for the nmr experiment.

The $K_4M(CN)_8 \cdot 2H_2O$ salts were prepared by literature procedures[30] and were purified by recrystallization; electronic spectra were in agreement with data reported in the literature.[31-33] These potassium salts were converted to the tetra-*n*-propylammonium salts by passage through an acid ion-exchange column, followed by neutralization with tetra-*n*-propylammonium hydroxide. The resultant solution was taken to dryness, and the salts were recrystallized three times from dichloromethane–diethyl ether and then vacuum dried.

The electronic spectra of $[(n\text{-}C_3H_7)_4N]_4Mo(CN)_8$ in water and in dichloromethane were nearly identical and very similar to those of the potassium salt in water.[31-33] The strong CN infrared stretch for this ammonium salt was at 2105 and 2090 cm^{-1} in H_2O and dichloromethane, respectively, as compared to 2106 cm^{-1} for the potassium salt in water. The electronic spectra of $[(n\text{-}C_3H_7)_4N]_4W(CN)_8$ in water and in dichloromethane were the same and the infrared CN stretch was at 2100 cm^{-1} (H_2O) and 2088 cm^{-1} (CH_2Cl_2) as compared to 2101 cm^{-1} for the potassium salt in H_2O. There was, however, no correspondence between the electronic spectrum of the butylammonium salt and the potassium salt: λ_{max} (Å) [ϵ (M^{-1} cm^{-1})] values are 3570 [918], 3400 [791], 2480 [4500], 2050 [5930] in H_2O and 3600 [764], 3400 [748], 2570 [2340], 2450 [2560] in CH_2Cl_2. The $[(n\text{-}C_3H_7)_4N]_4W(CN)_8$ salt was reconverted, essentially quantitatively, to $K_4W(CN)_8 \cdot 2H_2O$ by passage through a strong acid ion-exchange column and neutralization with KOH.

Nmr Studies. Proton nmr spectra were run over the temperature ranges +25 to −50° and +25 to −110° with a Varian HR-220 spectrometer and Varian HA-100, respectively. The ^{13}C spectra (^1H decoupled) were observed over the range +25 to −140° using a Bruker HFT-90 spectrometer with Digilab FTS/NMR-3 accessory (fluorine lock or deuterium lock). Temperatures for the spectra from the HR-220 were measured by observing the chemical shift separation in methanol or ethylene glycol samples. For the HFT-90, temperatures were measured with a copper-constantan thermocouple located just below the sample tube and were calibrated using a similar thermocouple held coaxially in the spinning-sample tube. In all *n*-propyl derivatives, the spectra are those expected for an AA′BB′C$_3$ spin system. The CH_2–N proton resonance is a complex triplet and is unaffected by irradiation at the CH_3 proton resonance frequency ($J_{CH_2(N)CH_3} < 1$ Hz). The internal methylene resonance is a sextet (near equivalence of $J_{CH_3\text{-}CH_2}$ and $J_{CH_2\text{-}CH_2}$). Irradiation at the CH_3 resonance frequency gives a complex triplet, and irradiation at the CH_2 resonance frequency gives a quartet. Sample spectral parameters are given in Table I.

Registry No. $K_4Mo(CN)_8$, 17456-18-7; $K_4W(CN)_8$, 17475-73-9; $[(n\text{-}C_4H_9)_4N]_4Mo(CN)_8$, 40678-64-6; $[(n\text{-}C_3H_7)_4N]_4Mo(CN)_8$, 40678-65-7; $[(n\text{-}C_3H_7)_4N]_4W(CN)_8$, 40678-66-8; $Ti[S_2CN(C_2H_5)_2]_4$, 29058-74-0; $Zr[S_2CN(C_2H_5)_2]_4$, 40678-68-0; $Nb^{IV}[S_2CN(C_2H_5)_2]_4$, 40674-61-1; $Ti[S_2CN(CH_2CH_2CH_3)_2]_4$, 40678-69-1; $Zr[S_2CN(CH_2CH_2CH_3)_2]_4$, 40788-52-1; $Nb^{IV}[S_2CN(CH_2CH_2CH_3)_2]_4$, 40674-62-2; $Zr[S_2CN(C_2H_5)_2]_x[S_2CN(n\text{-}C_3H_7)_2]_{4-x}$, $x = 1$, 40678-70-4; $Zr[S_2CN(C_2H_5)_2]_x[S_2CN(n\text{-}C_3H_7)_2]_{4-x}$, $x = 2$, 40678-71-5; $Zr[S_2CN(C_2H_5)_2]_x[S_2CN(n\text{-}C_3H_7)_2]_{4-x}$, $x = 3$, 40678-72-6.

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