Another measure of the extent of the metal–metal interaction in mixed-valence ions is the intensity of the IT band. With the Hush model, as the ground-state electronic interaction between the two metal ions increases, the intensity of the IT band should increase.[14] Given in Table III are the extinction coefficients for the IT bands and the corresponding oscillator strengths.

In contrast to the $\Delta G_{\text{com}}$ measurements, the intensity measurements indicate that differences in metal–metal interaction do exist for the mixed-valence complexes. The trend of the increasing interaction with increasing electron density about the metal center is followed up to the 4,7-dimethyl-1,10-phenanthroline complex. The 3,4,7,8-tetramethyl-1,10-phenanthroline complex unexpectedly breaks the pattern. Models indicate a possible steric problem with crowding between the 3(8) methyl group on one ruthenium site and the 3(8) methyl group on the other ruthenium site in this complex. The difficulty, however, does not appear to be overly severe, specifically, not sufficiently severe to cause significant deviation from any ruthenium–pyrazine–ruthenium orientation that could exist for the other mixed-valence complexes.

Although the intensity studies suggest differences in the extent of metal–metal interaction in these complexes, the differences are apparently not of sufficient magnitude to be reflected in differences in $\Delta G_{\text{com}}$. The contribution to $\Delta G_{\text{com}}$ due to stabilization by electronic delocalization can be estimated with use of method developed by Taube and co-workers.[11] With this procedure, resonance stabilization of the [2,3] species can be estimated to be very small and to vary from 52 cal/mol (2.3 mV) for the [(nitrophen)$_2$ClRu(pyz)RuCl(nitrophen)$_2$]$^{3+}$ complex to 89 cal/mol (3.9 mV) for [(dimethylphen)$_2$ClRu(pyz)RuCl(dimethylphen)$_2$]$^{3+}$.[17] Such small differences in resonance interactions (~2 mV) would be undetectable in making determinations of $\Delta G_{\text{com}}$ values.[18]

Although the amount of electron density on the ruthenium centers is being varied in the series of mixed-valence complexes, the variation does not cause overly dramatic increases or decreases in the extent of metal–metal interaction. The valence electrons on the ruthenium centers are in the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals. One, or more, of these orbitals is of appropriate symmetry to overlap with the $\pi$ system of the bridging pyrazine, which is thought to be the pathway for metal–metal interactions in these complexes. As discussed above, the variation in electron density in the series arises through variation in the $\sigma$-donor ability of the various phenanthroline ligands. To a reasonable approximation, the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals are not of appropriate symmetry to interact significantly with the $\sigma$ orbital on the nitrogen donating the pair of electrons from the ligand. Since the $\pi$-accepting abilities of the various ligands apparently are similar, the $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals may be at very similar energies in all the complexes. If so, the interaction of the $d_{xy}$, $d_{yx}$, and $d_{xz}$ orbitals with the $\pi$ system of pyrazine will be similar for all complexes, resulting in only small differences in metal–metal interaction. Instead of using ligands which have a variable $\sigma$-donor ability, it may be more appropriate to use ligands which have a variable $\pi$-donor ability (such as dithiocarbamates)[20] to cause significant changes in ruthenium–ruthenium interaction in complexes like these.

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**Registry No.** [(nitrophen)$_2$Ru(pyz)Cl](ClO$_4$), 76529-22-1; [(phen)$_2$Ru(pyz)Cl](ClO$_4$), 76529-24-3; [(dimethylphen)$_2$Ru(pyz)Cl](ClO$_4$), 76514-56-2; [(tetramethylphen)$_2$Ru(pyz)Cl](ClO$_4$), 76514-58-4; [(nitrophen)$_2$ClRu(pyz)RuCl(nitrophen)$_2$](ClO$_4$)$_2$, 76514-60-8; [(phen)$_2$ClRu(pyz)RuCl(phen)$_2$](ClO$_4$)$_2$, 76514-62-0; [(dimethylphen)$_2$ClRu(pyz)RuCl(dimethylphen)$_2$](ClO$_4$)$_2$, 76514-64-2; [(tetramethylphen)$_2$ClRu(pyz)RuCl(tetramethylphen)$_2$](ClO$_4$)$_2$, 76514-66-4; [(nitrophen)$_2$ClRu(pyz)RuCl(nitrophen)$_2$](ClO$_4$)$_4$, 76514-68-6; [(phen)$_2$ClRu(pyz)RuCl(phen)$_2$](ClO$_4$)$_4$, 76514-70-0; [(dimethylphen)$_2$ClRu(pyz)RuCl(dimethylphen)$_2$](ClO$_4$)$_4$, 76514-72-2; [(tetramethylphen)$_2$ClRu(pyz)RuCl(tetramethylphen)$_2$](ClO$_4$)$_4$, 76514-74-4; [(nitrophen)$_2$ClRu(pyz)RuCl(nitrophen)$_2$]$^{3+}$, 76549-97-8; [(phen)$_2$ClRu(pyz)RuCl(phen)$_2$]$^{3+}$, 76549-98-9; [(dimethylphen)$_2$ClRu(pyz)RuCl(dimethylphen)$_2$]$^{3+}$, 76549-99-0; [(tetramethylphen)$_2$ClRu(pyz)RuCl(tetramethylphen)$_2$]$^{3+}$, 76550-00-0; (phen)$_2$RuCl$_2$, 15453-59-5; (tetramethylphen)$_2$RuCl$_2$, 68510-56-5; (nitrophen)$_2$RuCl$_2$, 76514-75-5; (dimethylphen)$_2$RuCl$_2$, 76514-76-6; nitrophen, 4199-88-6; phen, 66-71-7; dimethylphen, 3248-05-3; tetramethylphen, 1660-93-1; [(nitrophen)$_2$Ru(pyz)Cl](ClO$_4$)$_2$, 76514-78-8; [(phen)$_2$Ru(pyz)Cl](ClO$_4$)$_2$, 76514-80-2; [(dimethylphen)$_2$Ru(pyz)Cl](ClO$_4$)$_2$, 76514-82-4; [(tetramethylphen)$_2$Ru(pyz)Cl](ClO$_4$)$_2$, 76514-84-6.

**Supplementary Material Available:** Analytical data for the ruthenium phenanthroline compounds (1 page). Ordering formation is given on any current masthead page.

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[14] The Hopfield[15] and "PKS"[16] models for mixed-valence complexes also develop the same relationship.

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[17] Resonance stabilization of [(phen)$_2$ClRu(pyz)RuCl(phen)$_2$]$^{3+}$ and [(tetramethylphen)$_2$ClRu(pyz)RuCl(tetramethylphen)$_2$]$^{3+}$ were estimated as 81 cal/mol (3.5 mV) and 69 cal/mol (3.0 mV), respectively. The values were calculated from the data in Table III, on the assumption $d$ (the distance between the metal ions) = 6.9 Å[3] and the bandwidths ($\Delta\nu_{1/2}$) $4.5 \times 10^3$ (nitrophen complex,) $5.0 \times 10^3$ (phen complex), $4.7 \times 10^3$ (dimethylphen complex), and $4.7 \times 10^3$ cm$^{-1}$ tetramethylphen complex).

[18] $\Delta G_{\text{com}}$ is determined from the relationship $\Delta G_{\text{com}} = E_{1/2}(2) - E_{1/2}(1)$.[19] Since experimental error in determining the $E_{1/2}$ values may be as high as ±10 mV, differences in resonance interactions less than 10 mV would be difficult to accurately determine.

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# X-ray Photoelectron Spectra of Inorganic Molecules. 28.[1] Sulfur 2p Binding Energies of Molybdenum Complexes Believed To Contain a Coordinated Partial Disulfide Bond

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From previous X-ray photoelectron spectra (XPS) measurements,[3-9] the binding of thioether and thiolate moieties to metal ions (M←SR$_2$ and M—SR coordination, respectively)

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[1] (a) Part 27: Walton, R. A. *Inorg. Chem.*, **1980**, *19*, 1100. (b) The present paper is Contribution No. 750 from the Charles F. Kettering Research Laboratory.

[2] (a) Purdue University. (b) Charles F. Kettering Research Laboratory.

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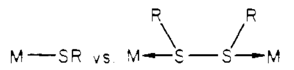
Table I. Core Electron Binding Energies of Sulfur-Containing Complexes of Molybdenum[a]

| no. | compd | Mo $3d_{5/2}$[b] | S $2p_{3/2}$[c] | N 1s | source |
|---|---|---|---|---|---|
| I | $\mathrm{MoO_2[SC(CH_3)_2CH_2NH_2]_2}$ | 231.6 (1.1) | 161.8 (1.2) | 399.5 | this work |
| II | $\mathrm{MoO_2[SC(CH_3)_2CH_2NHCH_3]_2}$ | 231.3 (1.6) | 161.7 (1.6) | 399.3 | this work |
| III | $\mathrm{MoO_2[SC(CH_3)_2CH_2N(CH_3)_2]_2}$[d] | 231.1 (1.7) | 161.7 (1.6) | 399.6 | this work |
| IV | $\mathrm{MoO_2[SC(CH_3)_2C(CH_3)_2NHCH_3]_2}$ | 231.5 (1.2) | 162.1 (1.4) | 399.8 | this work |
| V | $\mathrm{MoO_2[(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2]}$ | 231.2 (1.1) | 161.5 (1.1) | 399.4 | ref 8 |
| VI | $\mathrm{MoO_2[(SCH_2CH_2)_2NCH_2CH_2SCH_3]}$ | 231.4 (1.3) | 161.7 (1.1)<br>163.3 (1.1)[e] | 399.6 | ref 8 |
| VII | $\mathrm{Na_2\{Mo_2O_4[SCH_2CH(NH_2)CO_2]_2\}\cdot 5H_2O}$ | 231.1 (1.3) | 161.9 (1.4) | 399.6 | ref 8 |
| VIII | $\mathrm{Na_2\{Mo_2O_4[SC(CH_3)_2CH(NH_2)CO_2]_2\}\cdot 3H_2O}$ | 231.0 (1.2) | 161.6 (1.4) | 399.8 | ref 8 |
| IX | $\mathrm{Mo_2O_4[S_2CN(C_2H_5)_2]_2}$ | 231.5 | | | ref 15 |
| X | $\mathrm{Mo_2O_3(SC_6H_5)_2[S_2CN(C_2H_5)_2]_2}$ | 231.1 | | | ref 15 |
| XI | $\mathrm{[(C_4H_9)_4N]_2Mo_2O_2S_2[S_2C_2(CN)_2]_2}$ | 230.5 | | | ref 15 |
| XII | $\mathrm{[(C_2H_5)_4N]_2Mo_2S_4(SCH_2CH_2S)_2}$ | 228.9 (2.2) | 161.3[f] | 401.5 | this work |
| XIII | $\mathrm{[(C_2H_5)_4N]_2Mo_2S_4(SC_6H_5)_4}$ | 228.9 (1.6) | 161.2[f] | 401.7 | this work |
| XIV | $\mathrm{[(C_4H_9)_4N]_2Mo_2S_4(SC_6H_5)_4}$ | 229.1 (1.8) | 161.4[f] | 401.7 | this work |
| XV | $\mathrm{(CH_3)_2NCH_2CH_2SSCH_2CH_2N(CH_3)_2\cdot 2HCl}$[g,h] | | 162.9 (1.6) | 400.8 | this work |
| XVI | $\mathrm{(CH_3)_2NCH_2C(CH_3)_2SSC(CH_3)_2CH_2N(CH_3)_2\cdot 2HCl}$[g,h] | | 163.1 (1.6) | 401.1 | this work |

[a] Binding energies are internally referenced to a C 1s energy of 285.0 eV; full-width half-maximum values (fwhm) are given in parentheses for the Mo 3d and S 2p peaks. [b] The Mo $3d_{3/2}$ component is located at approximately 3.1 eV to higher energy. [c] The S $2p_{1/2}$ component is located at approximately 1.0 eV to higher energy. [d] Spectrum recorded at an X-ray power of 600 W rather than the more usual 1 kW, since sample decomposition occurred under the latter conditions. [e] S $2p_{3/2}$ binding energy of the thioether sulfur atom. [f] S 2p spectrum less well resolved than the other compounds studied. The S $2p_{3/2}$ energy quoted is that for the maximum of the band envelope (see text). [g] Spectrum recorded with use of a cold-probe maintained at 225 K. [h] Cl $2p_{3/2}$ binding energy at 196.4 eV (XV) or 196.8 eV (XVI).

is usually characterized by quite different S 2p chemical shifts relative to the free thioether and thiol ligands. Namely, a small positive chemical shift occurs in the case of thioethers while a negative chemical shift occurs with thiolate ligands.[10] Among the systems of previous interest to us[8] were several high-oxidation-state molybdenum complexes, specifically the molybdenum(V)–cysteine and –penicillamine species $\mathrm{Na_2\{Mo_2O_4[SCH_2CH(NH_2)CO_2]_2\}\cdot 5H_2O}$ and $\mathrm{Na_2\{Mo_2O_4[SC(CH_3)_2CH(NH_2)CO_2]_2\}\cdot 3H_2O}$ and the Mo(VI) complexes of stoichiometry $\mathrm{MoO_2[(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2]}$ and $\mathrm{MoO_2[(SCH_2CH_2)_2NCH_2CH_2SCH_3]}$ derived from the tetradentate tripod ligands $\mathrm{(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2}$ and $\mathrm{CH_3SCH_2CH_2N(CH_2CH_2SH)_2}$. Of note was a particularly large negative chemical shift (1.3–1.6 eV) which characterized the binding of thiols to molybdenum.

The XPS of coordinated disulfide ligands are, on the other hand, little studied[11,12] in spite of the potential use of the XPS technique in distinguishing this coordination mode from that of a metal–thiol unit in molecules where there is ambiguity concerning the nature of the metal–ligand bonding, viz.



As a part of our interest in the XPS of molecules which might exhibit transition metal–RSSR bonding,[1a,9] we have now measured, and report herein, the spectra of several cysteamine type complexes of Mo(VI), which were recently prepared and characterized.[13] These complexes contain the $\mathrm{R_1R_2NC(R_3)_2C(R_4)_2S^-}$ ligands, where $R_{1,2,3,4}$ = H or $CH_3$, and are of stoichiometry $\mathrm{MoO_2L_2}$. The complexes $\mathrm{MoO_2[SC(CH_3)_2CH_2NHCH_3]_2}$[13] ($R_1 = R_3 = H$, $R_2 = R_4 = CH_3$), $\mathrm{MoO_2[SC(CH_3)_2C(CH_3)_2NHCH_3]_2}$[14] ($R_1 = H$, $R_2 = R_3 = R_4 = CH_3$), and $\mathrm{MoO_2[SC(CH_3)_2CH_2N(CH_3)_2]_2}$[14] ($R_1 = R_2 = R_4 = CH_3$, $R_3 = H$) have been shown to possess an unusual six-coordination sphere describable as a skew trapezoidal bipyramid (e.g., Figure 1). However, in the present context the structural feature of more interest is the $S_1$–$S_2$ distance of 2.7–2.8 Å in these complexes, which implies the formation of a partial S–S bond within the Mo coordination sphere.[13,14] A question of considerable importance is whether XPS measurements can provide any evidence for a disulfide unit and the presence of molybdenum in an oxidation state lower than +6 in these complexes and, indeed, in other complexes of this type.[13,14]

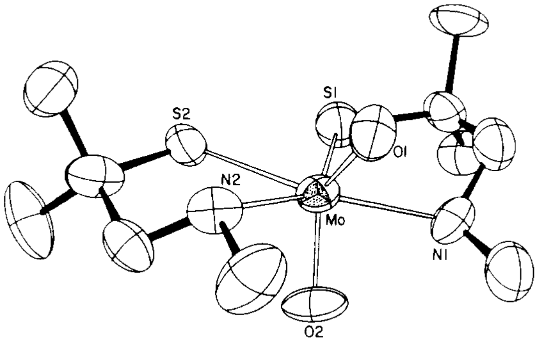


**Figure 1.** Structure of $\mathrm{MoO_2[SC(CH_3)_2CH_2NHCH_3]_2}$ (based upon that given in ref 13). All unlabeled atoms are carbon.

The Mo 3d, S 2p, and N 1s binding energies of the cysteamine complexes, together with related data for several molybdenum complexes which are important for comparative purposes, are presented in Table I. Some of the latter data are taken from published work.[8,15] For data reported herein for the first time, all samples were, with one exception, free of X-ray damage. In the case of complex III, X-ray decomposition was prevented by use of an X-ray beam power lower than that we routinely use (600 W rather than 1000 W). The sublimation of the disulfide salts XV and XVI, a problem at

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(10) Note that comparison in the case of thioethers is between $\mathrm{M \leftarrow SR_2}$ and $\mathrm{SR_2}$, whereas for thiolate ligands we compare M—SR and HSR, i.e., the effect of $M^{n+}$ vs. $H^+$ coordination upon the S 2p binding energies of $^-$SR.

(11) The Zn(II) and Cd(II) complexes of the organic disulfide cystine have S 2p binding energies of 163.0 and 162.8 eV, respectively. These are essentially unchanged from that of the free ligand which is not surprising since neither complex contains metal–sulfur bonds.[6,12] On the other hand, bis($\mu$-cystinato)-dicopper(II), which unlike the Zn and Cd derivatives may actually involve weak M–S coordination, has its S 2p energy located at 163.7 eV.[7]

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room temperature, was thwarted by use of a sample cold-probe held at 225 K.

The most striking feature of the Mo 3d, S 2p, and N 1s binding energies of the cysteamine complexes I–IV is their similarity to the comparable data for the structurally characterized[16,17] complexes V and VI, which contain coordination spheres very similar to I–IV but lack the postulated coordinated disulfide bond. More importantly, the binding energy difference $E_B(\text{Mo } 3d_{5/2}) - E_B(\text{S } 2p_{3/2})$ is seen to be essentially the same for all six complexes ($69.6 \pm 0.2$ eV), implying that there is no XPS evidence for a significant degree of dithiolate–disulfide oxidation and concomitant increase in electron density at the metal for any of the complexes I–IV. Thus, these cysteamine complexes appear to be typical dioxomolybdenum(VI)–thiolate derivatives within the limits of energy resolution available to us with the XPS technique. In addition to the S 2p binding energies of I–IV being characteristic of molybdenum–thiolate coordination,[8] they are clearly very different from the corresponding energies of the disulfide salts XV and XVI (Table I) and are likewise much lower than the S 2p energies expected for metal complexes of disulfides.[11]

We have been careful in considering the Mo 3d binding energies of I–IV to restrict our comparisons to those molybdenum complexes that contain ligand sets very similar to the ones possessed by I–IV, i.e., complexes V and VI. The importance of this is illustrated by the changes in the Mo 3d core binding energies which occur within the series of Mo(V) complexes VII–XIV (Table I). Four of these complexes (VII–X) exhibit Mo 3d binding energies that are very similar to those of the Mo(VI) derivatives in Table I, but since they possess different structures and contain ligands different from those of complexes I–VI, such coincidences are not particularly significant, at least as far as our analysis is concerned. However, as the oxygen atoms in the oxomolybdenum(V) complexes become increasingly substituted by sulfur, the Mo 3d energies decrease by as much as 2 eV. This reflects the increasing polarizability of sulfur relative to oxygen and the resultant decrease in positive charge at the metal center.

The lack of change in S 2p and Mo 3d binding energies in the complexes with the short S–S distance [as compared to conventional octahedral dioxomolybdenum bis(thiolate) complexes] indicates a relatively small net charge transfer in the complexes of unusual structure compared with the charge transfer in those of conventional structure. However, this does not necessarily preclude the previous designation[13] of a partial S–S bond. Thus, at 2.7–2.8 Å the degree of disulfide bond formation is, at best, small, leading to a possibly negligible charge transfer. Further, to the extent that the partial S–S bond is formed, the resultant side-on bound disulfide, as in Müller's $S_2^{2-}$ complexes,[18] could undergo a synergic bonding by donating electron density to the metal through $\sigma_b$ while simultaneously accepting electron density into $\sigma^*$ orbitals. The result of such interactions could either increase or decrease electron density on sulfur and Mo and hence cancel any change in S 2p or Mo 3d binding energy caused by the postulated intramolecular redox.

A final point concerns the S 2p spectrum of the sulfur-rich complexes XII–XIV, which contain, in addition to thiol ligands, both terminal Mo═S and bridging Mo—S—Mo bonds. While the S $2p_{1/2,3/2}$ band envelopes of these complexes are slightly broader than those of complexes I–IV (fwhm values are 2.7–2.6 eV vs. 2.4–2.0 eV), it is apparent that the binding energies of the terminal and bridging sulfur atoms and the sulfur atoms of the thiol ligands are very close to one another. This result is similar to that reported[19] for the iron complex $[(C_2H_5)_4N]_2[Fe_4S_4(SCH_2C_6H_5)_4]$, which displays only a single S 2p photoline (at 161.8 eV) despite its possession of two different sulfur environments. However, its breadth (fwhm = 2.7 eV) indicates that as with the situation we find for $Mo_2S_4(SR)_4^{2-}$, the binding energies of the sulfide and thiolate sulfur atoms are very similar although not coincident (the chemical shift is probably 0.5 eV or less.)[20]

## Experimental Section

**Spectral Measurements.** A Hewlett-Packard Model 5950A ESCA spectrometer was used to record the X-ray photoelectron spectra. An electron "floodgun" was used to reduce to a minimum surface-charging effects. Full details of the experimental procedure are described elsewhere.[23,24]

**Preparation of Metal Complexes and Disulfides.** Complexes I–VI were prepared by the reaction[13]

$$MoO_2(acac)_2 + 2LH \xrightarrow{CH_3OH} MoO_2L_2 + 2acacH$$

where 2LH and $L_2$ represent respectively the neutral and the anionic forms of the bidentate ligands (in I–IV) and the tetradentate ligands (in V and VI) and acac = acetylacetonate. Complete synthetic details and other physical properties will appear elsewhere.[25]

Complex XIII was prepared by the reaction of $[NH_4]_2[Mo_2(S\text{-}S)_6]\cdot 2H_2O$[18] with 30 equiv of the sodium salt of thiophenol in acetonitrile containing $(C_2H_5)_4N^+Br^-$. The product was precipitated by slow addition of 2-propanol. Complex XII was prepared in a similar manner by the reaction of $[NH_4]_2[Mo_2(SS)_6]\cdot 2H_2O$ with 25 equiv of the disodium salt of 1,2-dimercaptoethane in $CH_3OH$, followed by the addition of $(C_2H_5)_4N^+Br^-$. Complex XIV was prepared by the same procedure as XIII using $(C_4H_9)_4N^+Br^-$ as the source of cation rather than $(C_2H_5)_4N^+Br^-$. All complexes gave satisfactory elemental and spectroscopic analyses. Full synthetic details and description of physical properties of XII–XIV will appear elsewhere.[26] The disulfides of compounds XV and XVI were prepared according to the methods described in ref 27 and 28, respectively. The hydrochloride salts, XV and XVI, were prepared by the addition of 2 equiv of concentrated HCl in 2-propanol to a hot 2-propanol solution containing 1 equiv of the disulfide. A white crystalline solid separated upon cooling to 0 °C. The product was filtered, washed with cold 2-propanol and $(C_2H_5)_2O$, and dried under vacuum. Anal. Calcd for $C_8H_{22}N_2S_2Cl_2$: C, 34.16; H, 7.88; N, 9.96. Found: C, 34.27; H, 8.20; N, 9.75. Calcd for $C_{12}H_{30}N_2S_2Cl_2$: C, 42.72; H, 8.96; N, 8.30. Found: C, 42.66; H, 9.14; N, 8.08.

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**Registry No.** I, 76757-49-8; II, 74005-67-7; III, 74005-68-8; IV, 76772-96-8; XII, 63447-82-5; XIII, 76757-51-2; XIV, 76757-52-3; XV, 17339-60-5; XVI, 76758-29-7.

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