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Ionization Studies of Mixed-Ligand Copper(II) Complexes

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Received May 5, 1977

As discussed in a recent review by Westmore[1] there is an ambiguity concerning the nature of the orbital that contributes the electron which is removed in ionization studies of β-diketonates of copper(II). Electron spin resonance (ESR) studies have clearly shown that the orbital containing the unpaired electron is composed mainly of a copper in-plane σ d orbital.[2] In the classical description of bonding this half-filled orbital would also be the least stable occupied orbital. However, the lowest energy ionization process observed in photoelectron and/or mass spectra studies has generally been thought to arise from a ligand-based out-of-plane π orbital.[5] Experimental interpretations of this type have been used to justify molecular orbital calculations which placed the molecular orbitals with predominant metal d-orbital character in more stable energy levels than some of the molecular orbitals which are primarily ligand in composition. Jorgensen, who has been one of the advocates of this reversal of the classical filling order,[3,4] terms this model the "third revolution in ligand field theory".[3]

One experimental measurement which did not fit the model invoking ionization of the ligand π system is the ionization potential (IP) of the mixed-ligand complex Cu(acac)(hfacac).[6,7] The IP was not similar to that of the complex composed of the less stable ligands but was close to the mean of the IPs of the complexes containing the two nonmixed chelates. Our ESR data[8] indicated that the hyperfine splitting data for the σ orbital containing the unpaired electron behaved in a similar fashion. Our theoretical calculations of the σ orbital ionization potentials for $Cu(acac)_2$, Cu(acac)(hfac), and $Cu(hfac)_2$ also predicted the mean behavior for Cu(acac)(hfac).[9] However, a single experimental and theoretical exception does not make a very convincing argument. We have therefore experimentally and theoretically determined the ionization potentials for a number of our mixed-ligand complexes.

Procedure

The experimental ionization potentials were obtained on a Consolidated Electrodynamics Corp. 21-110C double focusing high-resolution mass spectrometer. The extrapolated voltage difference method[11] was used with argon (15.76 eV) as the calibrating gas standard.[12] The theoretical ionization potentials were obtained by the use of the extended Hückel method as described previously.[9]

Results and Discussion

Levitt and Levitt[10] reported that the experimental ionization potentials for nonmixed Cu(II) β-diketonates were proportional to the sums of the Hammett σ_m substituent constants by the equation

$$\mathrm{IP}_{\mathrm{Cu-R}} = \mathrm{IP}_{\mathrm{Cu-H}} + a_m \Sigma\sigma_m \qquad (1)$$

The experimental data in Table I fit this equation with a slope, a_m, of 0.745 and an intercept, $\mathrm{IP}_{\mathrm{Cu-R}}$, of 8.53. The correlation has an r of 0.994 and a standard deviation of 0.07 eV. Since this correlation includes a number of both mixed and nonmixed complexes, there should no longer be any doubt concerning the inappropriateness of a model invoking simple ionization of the least stable ligand π system.

The following examination of the theoretical calculations indicates that the experimental data are consistent with an ionization from the metal d orbitals but are not consistent with either a ligand π or a ligand σ origin.

Table I. Ionization Potentials (eV) for $Cu(O\text{-}CR_1\text{-}CH\text{-}CR_2\text{-}O)_2$

R_1	R_2	R_1[a]	R_2[a]	IP (exptl)[b]	IP (calcd)[c]
CH_3	Thenoyl	CH_3	Thenoyl	8.17	
CH_3	CH_3	CH_3	CH_3	8.33	9.246
Phenyl	CH_3	Phenyl	CH_3	8.53	
Phenyl	Phenyl	Phenyl	Phenyl	8.72	
CH_3	CH_3	CH_3	CF_3	8.75	9.281
CH_3	Phenyl	Phenyl	CF_3	8.80	
CF_3	Thenoyl	CF_3	Thenoyl	9.05	
CH_3	Phenyl	CF_3	CF_3	9.09	
CH_3	CH_3	CF_3	CF_3	9.22	9.307
Phenyl	CF_3	Phenyl	CF_3	9.23	
CH_3	CF_3	CH_3	CF_3	9.33	9.318
Thenoyl	CF_3	CF_3	CF_3	9.44	
CH_3	CF_3	CF_3	CF_3	9.50	9.344
CF_3	CF_3	CF_3	CF_3	9.83	9.371

[a] R_1 and R_2 of the second ligand. [b] +0.05 eV (95% confidence figure using seven degrees of freedom). [c] From ref 9.

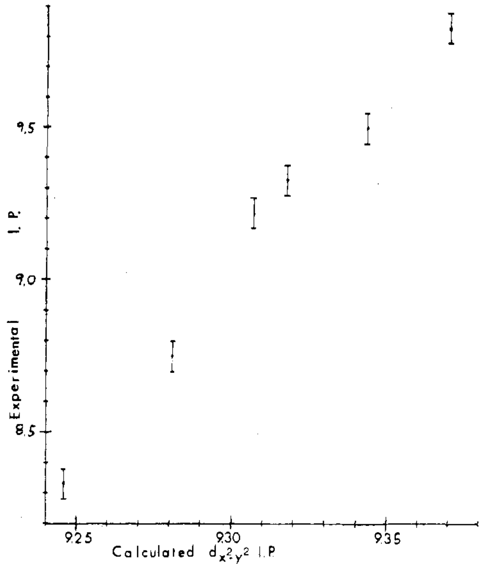

Figure 1. Plot of calculated $d_{x^2-y^2}$ ionization potentials vs. the experimental values. Data are from Table I.

A plot of the experimental metal d orbital IP vs. the theoretical, extended Hückel calculated values is given in Figure 1. This correlation indicates that the metal d orbital containing the unpaired electron does have the correct qualitative substitutent dependence to explain the experimental IP data. Quantitatively, the theoretical dependence on substitutent is an order of magnitude less than the experimental dependence. Since constant sets of H_{ii} values and x, y, z coordinates were used for the series, this "buffering" of the theoretical dependence is not unexpected.

The calculated energy behavior of the highest occupied *ligand-based* orbitals is given in Table II. The two ligands in the nonmixed complexes form symmetrical, completely mixed ligand-based molecular orbitals while the two ligands in the mixed complexes form separate molecular orbitals for each ligand. In addition the energies of the least stable occupied ligand-based orbitals in the mixed complexes are about the same (±0.1 eV or less) as the energies of the *corresponding* orbitals in the nonmixed complexes. Are these results meaningful or are they the result of using too crude a theoretical method? The extended Hückel method is an approximate method; however, there does not appear to be any evidence that it fails on such a basic prediction as to whether a group of atomic orbitals will form or not form a set of molecular orbitals. The magnitude of the coefficients and the

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Table II. Energies[d] and Origins of the Four Highest Energy Occupied *Ligand Based*[f] Orbitals

Complex				Origin of the molecular orbital[e]					
				F, F ligand		H, F ligand		H, H ligand	
R_1	R_2	R_1[a]	R_2[a]	π	σ	π	σ	π	σ
F	F	F	F	−11.922	−12.785				
				−11.922	−12.849				
H	F	F	F	−11.922	−12.817	−12.256	−12.253		
H	F	H[b]	F[b]			−12.235	−12.167		
						−12.276	−12.340		
H	F	H[c]	F[c]			−12.220	−12.221		
						−12.294	−12.284		
H	H	F	F	−11.922	−12.818			−12.498	−11.940
H	H	H	F			−12.251	−12.279	−12.504	−11.913
H	H	H	H					−12.450	−11.795
								−12.547	−12.085

[a] R_1 and R_2 of the second ligand. [b] The fluorines are trans to each other. [c] The fluorines are cis to each other. [d] In units of eV. Data from the same extended Hückel calculation used in ref 9. [e] In the nonmixed complexes each orbital is symmetrically distributed over both ligands. In the mixed complexes the orbital is mainly localized on the indicated ligand. [f] The predominantly metal d orbitals are not included in this table. They are all less stable than the ligand based orbitals.

energies may change slightly from method to method but the above gross mixing or nonmixing information should not. Also of interest is the prediction that F substitution stabilizes the σ-ligand system but *destabilizes* the π-ligand system. Thus, the predicted effect of F substitution upon the π energy level is in the wrong direction to be correlated with the experimental IP values. Can the predicted behavior be supported by other experimental data such as optical spectroscopy? Fackler et al.[17] have shown that CF_3 substitution in β-diketonates of Cu(II) lowers the energy of the $\pi \rightarrow \pi^*$ transition and raises the energy of the $\sigma \rightarrow \sigma^*$ transition in agreement with our predicted behavior. In fact, Lintvedt and Kernitsky[18] have shown the same experimental behavior for tris(iron(III))–acetylacetone complexes. Unfortunately, the J and K electron integrals also effect the observed optical transition energies,[13] so that one *cannot* say for certain that if $\pi \rightarrow \pi^*$ is decreasing this means that the π energy level is becoming less stable. In fact, in some unpublished CNDOS[19] studies of the enol form of substituted acetylacetone we find the opposite behavior. This is a point for which the extended Hückel method may be unreliable.

The similarity of the metal complex IP to the corresponding free ligand IP has been interpreted as support for the π origin assignment for the metal complex.[1] However, back in 1973, Houk et al.[16] used the CNDO/2 method to assign the photoelectron spectrum of the H-bonded enol form of acetylacetone and they found, contrary to previous predictions, that the lowest energy ionization originated from an oxygen lone pair, not from the out-of-plane π orbital!

Westmore[1] proposed that the mixed-ligand behavior may be explained by assuming that "the observed IP does not correspond exclusively to ionization from a particular orbital, though it would probably be weighted in favor of ionization from a ligand π_3 orbital". He also felt that, even if the metal orbitals were the least stable, their ionization would not be observed because their ionizations are, in a sense, "forbidden ionizations" due to a required shortening of the metal–ligand bonds upon removal of an antibonding d electron. The data available to him supported this theory. However, two recent photoelectron studies of nickel–acetylacetonate type complexes have observed ionizations at energies lower than those detected in mass spectrum electron impact studies. The new peaks were assigned to the ionizations due to the removal of d electrons. For Ni(acac)$_2$, Brittain and Disch[14] assigned two peaks at 7.61 and 8.29 eV as d ionizations and assigned the first π ionization at 8.52 eV. Cauletti and Furlani[15] assigned three peaks at 7.41, 7.89, and 8.15 eV as d ionizations and assigned the first π ionization at 8.44 eV. The literature mass spectrum ionization potential is 8.23 eV[1] while our unpublished value using the same technique as in the present paper is 8.13 eV. Because of the large differences in data from group to group and technique to technique, the question of whether the mass spectral technique is insensitive to d orbital ionizations *for Ni(acac)$_2$* remains unanswered. However, one of the above photoelectron investigations[14] also looked at some copper acetylacetonate type complexes and found no additional peaks at lower energies than those which had been found by mass spectral studies.

Conclusion

Even though the present data support a d orbital assignment, we feel that the data are not conclusive on this point. On the other hand, it appears premature to justify a "third revolution in ligand field theory" on a π ligand ionization assignment model.

Acknowledgment. The mixed-ligand complexes were prepared with National Science Foundation Grant GP9485 support. We wish to thank the Goodyear Tire and Rubber Co., Akron, Ohio, for making available their mass spectrometer facilities for this study.

Registry No. Cu(O-C(CH_3)-CH-C(thenoyl)-O)$_2$, 14409-22-4; Cu(O-C(CH_3)-CH-C(CH_3)-O)$_2$, 13395-16-9; Cu(O-C(phenyl)-CH-C(CH_3)-O)$_2$, 14128-84-8; Cu(O-C(phenyl)-CH-C(phenyl)-O)$_2$, 14405-48-2; Cu(O-C(CH_3)-CH-C(CH_3)-O)(O-C(CH_3)-CH-C(CF_3)-O), 21429-76-5; Cu(O-C(CH_3)-CH-C(phenyl)-O)(O-C(phenyl)-CH-C(CF_3)-O), 64626-98-8; Cu(O-C(CF_3)-CH-C(thenoyl)-O)$_2$, 13928-09-1; Cu(O-C(CH_3)-CH-C(phenyl)-O)(O-C(CF_3)-CH-C(CF_3)-O), 29066-88-4; Cu(O-C(CH_3)-CH-C(CH_3)-O)(O-C(CF_3)-CH-C(CF_3)-O), 21429-77-6; Cu(O-C(phenyl)-CH-C(CF_3)-O)$_2$, 14126-89-7; Cu(O-C(CH_3)-CH-C(CF_3)-O)$_2$, 14324-82-4; Cu(O-C(thenoyl)-CH-C(CF_3)-O)(O-C(CF_3)-CH-C(CF_3)-O), 29198-04-7; Cu(O-C(CH_3)-CH-C(CF_3)-O)(O-C(CF_3)-CH-C(CF_3)-O), 21429-78-7; Cu(O-C(CF_3)-CH-C(CF_3)-O)$_2$, 14781-45-4; Cu(O-C(F)-CH-C(F)-O)$_2$, 55519-81-8; Cu(O-C(H)-CH-C(F)-O)(O-C(F)-CH-C(F)-O), 55519-83-0; *trans*-Cu(O-C(H)-CH-C(F)-O)$_2$, 55529-80-1; *cis*-Cu(O-C(H)-CH-C(F)-O)$_2$, 55519-84-1; Cu(O-C(H)-CH-C(H)-O)(O-C(F)-CH-C(F)-O), 55519-82-9; Cu(O-C(H)-CH-C(H)-O)(O-C(H)-CH-C(F)-O), 55519-85-2; Cu(O-C(H)-CH-C(H)-O)$_2$, 23507-22-4.

References and Notes

(1) J. B. Westmore, *Chem. Rev.*, **76**, 695 (1976).
(2) H. A. Kuska and M. T. Rogers, *J. Phys. Chem.*, **71**, 109 (1967), and references cited therein.
(3) C. K. Jorgensen, *Struct. Bonding (Berlin)*, **22**, 49 (1975).
(4) C. K. Jorgensen, *Theor. Chim. Acta*, **34**, 189 (1974).
(5) S. Evans, A. Hamnett, A. F. Orchard, and D. R. Lloyd, *Discuss. Faraday Soc.*, **54**, 227 (1973).
(6) H. F. Holtzclaw, Jr., R. L. Lintvedt, H. E. Baumgartene, R. G. Parker, M. M. Bursey, and P. F. Rogerson, *J. Am. Chem. Soc.*, **91**, 3774 (1969).
(7) C. Reichert, J. B. Westmore, *Can. J. Chem.*, **48**, 3213 (1970).
(8) M. F. Farona, D. C. Perry, and H. A. Kuska, *Inorg. Chem.*, **7**, 2415 (1968).

(9) H. A. Kuska, *J. Am. Chem. Soc.*, **97**, 2289 (1975).
(10) B. W. Levitt and L. S. Levitt, *Coord. Chem.*, **3**, 187 (1973).
(11) J. W. Warren, *Nature (London)*, **164**, 810 (1950).
(12) F. A. White, "Mass Spectrometry in Science and Technology", Wiley, New York, N.Y., 1968, pp 343–345.
(13) H. H. Jaffe, D. L. Beveridge, and M. Orchin, *J. Chem. Educ.*, **44**, 383 (1967).
(14) H. G. Brittain and R. Disch, *J. Electron Spectrosc.*, **7**, 475 (1975).
(15) C. Cauletti and C. Furlani, *J. Electron Spectrosc.*, **6**, 465 (1975).
(16) K. N. Houk, L. P. Davis, G. R. Newkome, R. E. Duke, Jr., and R. V. Nauman, *J. Am. Chem. Soc.*, **95**, 8364 (1973).
(17) J. P. Fackler, Jr., and F. A. Cotton, *Inorg. Chem.*, **2**, 102 (1963).
(18) R. L. Lintvedt and L. K. Kernitsky, *Inorg. Chem.*, **9**, 491 (1970).
(19) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807, 4050 (1968); **49**, 1221 (1968); **50**, 1126 (1969); Program QCPE 174, Quantum Chemistry Program Exchange, Indiana University.

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A High-Yield Synthesis of Rhenium(III) Iodide and the Isolation and Characterization of β-Molybdenum(II) Iodide[1]

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Received July 27, 1977

We have recently demonstrated[2] that the metal acetates $Mo_2(O_2CCH_3)_4$, $Re_2(O_2CCH_3)_4X_2$, where X = Cl or Br, and $Rh_2(O_2CCH_3)_4$ exhibit different reactivities toward gaseous hydrogen chloride and hydrogen bromide. While $Mo_2(O_2CCH_3)_4$ reacts to afford β-MoX_2, and $Re_2(O_2CCH_3)_4X_2$ are converted to the trinuclear halides Re_3X_9, the related reactions of $Rh_2(O_2CCH_3)_4$ result in disproportionation to RhX_3 and rhodium metal. To complete our current studies on the reactions of the solid metal acetates with the gaseous hydrogen halides, we now report details of the reactions of hydrogen iodide with $Mo_2(O_2CCH_3)_4$ and $Re_2(O_2CCH_3)_4Cl_2$. This work has led to a convenient high-yield synthesis of Re_3I_9 and the isolation of the new molybdenum iodide phase β-MoI_2.

Experimental Section

Starting Materials. Molybdenum hexacarbonyl, potassium perrhenate, tertiary phosphines, and pyridine together with all reagent-grade solvents and gases were obtained from commercial sources. All solvents were deoxygenated by purging with nitrogen gas for at least 1 h prior to use.

Molybdenum(II) acetate, $Mo_2(O_2CCH_3)_4$, was prepared by the standard literature procedure,[3] while $Re_2(O_2CCH_3)_4Cl_2$ was prepared from $ReOCl_3(PPh_3)_2$ using our slight modification[2] of the method described by Rouschias and Wilkinson.[4]

Synthetic Procedures. (A) Reactions of Metal Acetates with Hydrogen Iodide. (i) $Mo_2(O_2CCH_3)_4$. Finely ground molybdenum(II) acetate (0.5 g), contained in a porcelain boat, was treated with hydrogen iodide gas for 6 h at 300 °C. The resulting dark brown powder was reground and reheated at 300 °C in a flow of HI gas for a further 6 h. The final product (0.8 g) was analytically pure β-MoI_2. Anal. Calcd for MoI_2: I, 72.6; Mo, 27.4. Found: I, 72.5; Mo, 27.9. Yield >95%.

(ii) $Re_2(O_2CCH_3)_4Cl_2$. Using a procedure similar to that described previously to prepare Re_3Cl_9 and Re_3Br_9,[2] the reaction of rhenium(III) acetate with hydrogen iodide gas for 5 h at 300 °C afforded black Re_3I_9. Anal. Calcd for Re_3I_9: I, 67.15. Found (for separate preparative samples): I, 66.8, 66.85. Yield ~80%.

(B) Reactions of β-MoI_2 with Pyridine and Tri-*n*-propylphosphine. (i) Pyridine. β-MoI_2 (0.3 g) and 20 mL of pure dry pyridine were refluxed together for 5 days. The reaction mixture was then cooled and filtered and the filtrate evaporated to dryness in vacuo. The resulting brown residue was washed with diethyl ether and dried. Microanalytical data showed that this was not a pure sample of $Mo_2I_4(py)_4$. Anal. Calcd for $C_{20}H_{20}I_4N_4Mo_2$: C, 23.6; H 2.0; I, 50.0. Found: C, 25.85; H, 2.3; I, 46.2. However, the infrared spectrum of this product in the 4000–400-cm^{-1} region was identical with that of the complexes $Mo_2X_4(py)_4$, where X = Cl or Br.[2] In the far-infrared region (400–200-cm^{-1}) bands at 252 (m) and 240 (w) cm^{-1} [probably assigned to ν(Mo–N)] have counterparts in the spectra of $Mo_2Cl_4(py)_4$ and $Mo_2Br_4(py)_4$ at 247 (m–w) and 240 (m) cm^{-1}, respectively.[2,5] The diffuse-reflectance and solution (pyridine) electronic absorption spectra exhibit a low-energy absorption at ~740 nm, in keeping with the trend established by $Mo_2Cl_4(py)_4$ and $Mo_2Br_4(py)_4$ which possess related low-energy bands at 560 and 680 nm, respectively.[2,5] Since the x-ray powder pattern of this product is not the same as that reported by Brencic et al.[6] for a sample of $Mo_2I_4(py)_4$ prepared by the reaction of pyridine with $(picH)_2Mo_2I_6(H_2O)_2$, where picH = 4-methylpyridinium, these two products may be different structural isomers.

(ii) Tri-*n*-propylphosphine. β-MoI_2 (0.3 g) was added to 15 mL of dry acetone followed by 1.0 mL of tri-*n*-propylphosphine and the resulting reaction mixture was refluxed for 1 day and then filtered while hot. The blue crystals of the complex $Mo_2I_4(P\text{-}n\text{-}Pr_3)_4$ (0.07 g) were washed with ethanol and diethyl ether and then dried in vacuo. Anal. Calcd for $C_{36}H_{84}I_4P_4Mo_2$: C, 32.3; H, 6.3; I, 37.9. Found: C, 32.2; H, 6.4; I, 37.9. Yield 12%.

(C) Reactions of Re_3I_9 with Tri-*n*-propylphosphine and Heterocyclic Tertiary Amines. (i) Tri-*n*-propylphosphine. Re_3I_9 (0.6 g) was dissolved in 15 mL of dry acetone. A small quantity of tri-*n*-propylphosphine (~1 mL) was added and the resulting solution was gently heated for 20 min and then cooled. The insoluble gray powder (0.19 g) was filtered off and washed with ethanol and diethyl ether and dried in vacuo. Anal. Calcd for $C_{36}H_{84}I_4P_4Re_2$: C, 28.4; H, 5.5; I, 33.4. Found: C, 27.9; H, 5.6; I, 33.5. Yield 24%. A molecular weight determination in benzene confirmed the dimeric nature of this complex. Calcd for $Re_2I_4(P\text{-}n\text{-}Pr_3)_4$: 1520. Found: 1645. The spectroscopic properties of this complex were identical in all respects with those exhibited by a complex of this same stoichiometry prepared by an alternative procedure.[7]

(ii) Pyridine, 4-Methylpyridine, and Pyrazine. Although chloride and bromide derivatives of the types $Re_3X_9L_3$ and $[Re_3X_6L_3]_n$ have been prepared from the direct reaction of Re_3X_9,[8,9] treatment of acetone solutions of Re_3I_9 with pyridine, 4-methylpyridine, and pyrazine did not produce the corresponding iodide complexes. In the case of the reactions with pyridine and 4-methylpyridine, infrared spectral data on the resulting impure brown solids support the formation of rhenium(V) species of the type $ReO_2L_4^+$ (ν(O=Re=O) at ~820 cm^{-1}).[10]

Physical Measurements and Analytical Procedures. These were carried out as described previously.[2]

Results and Discussion

The reaction of $Re_2(O_2CCH_3)_4Cl_2$ with hydrogen iodide at 300 °C to afford rhenium(III) iodide in high yield (~80%) is the most direct synthetic route available for this halide. This preparation offers considerable advantages over other literature methods,[11-16] in terms of both the reproducibility and simplicity of our procedure and the high product yield which is obtained. Also, since this same rhenium(III) acetate starting material can also be used for the synthesis of Re_3Cl_9 and Re_3Br_9,[2] this synthetic procedure is of quite general applicability.

There is good agreement between the x-ray powder pattern for Re_3I_9 prepared by our method and that reported by Bennett et al.[17] for a sample of this halide obtained by an alternative synthetic route. The x-ray photoelectron spectrum (ESCA) of this phase (Re $4f_{5/2,7/2}$ binding energies at 43.7 and 41.3 eV and I $3d_{3/2,5/2}$ energies at 630.7 and 619.2 eV) shows that it possesses considerably lower Re 4f binding energies than the analogous chloride and bromide phases.[2] This trend reflects the greater charge density at the metal center in Re_3I_9, relative to Re_3Cl_9 and Re_3Br_9, presumably a consequence of the lower electronegativity of iodine (I < Br < Cl).

As noted previously,[17] Re_3I_9 forms very few compounds. In the present work we have been unable to form complexes of the type $Re_3I_9L_3$ by direct reaction of this halide with either heterocyclic tertiary amines or tertiary phosphines. In contrast to the related behavior of Re_3Cl_9 and Re_3Br_9,[8,9,18,19] the decomposition of the Re_3I_9 cluster appears to be very rapid. In spite of this, the reactions of Re_3I_9 resemble those of the related chloride and bromide in one respect, namely, the formation of dimeric metal–metal bonded complexes of the type

0020-1669/78/1317-0200$01.00/0