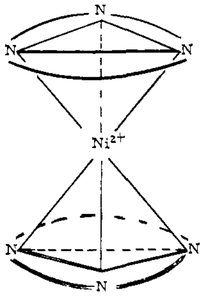
extreme labilization of the organic substrate, terminating in formation of a stable product. In the self-condensation reaction, the yield of copper(II) complex of tetrameric ligand slightly exceeds the combined yields of the nickel(II) complexes of trimeric and tetrameric ligands.

This metal ion induced rearrangement has been used to synthesize a complex containing two trimeric condensates bound to each nickel ion. This compound is prepared by heating a suspension of 2 equiv of the quinazoline in methanol with 1 equiv of nickel(II) nitrate for 2 hr under reflux. The quinazoline dissolves with reaction, first giving an orange-yellow colored solution which slowly turns wine-red. When the homogeneous solution cools to room temperature, red-brown clusters of needles of bis(tribenzo[*b*,*f*,*j*]-[1,5,9]triazacycloduodecine)nickel(II) nitrate monohydrate are deposited on the walls of the reaction vessel. *Anal.* Calcd for $Ni(C_{21}H_{15}N_3)_2(NO_3)_2 \cdot H_2O$: C, 61.56; H, 3.94; N, 13.68. Found: C, 61.63; H, 4.01; N, 13.45. The infrared spectrum of $Ni(TRI)_2(NO_3)_2 \cdot H_2O$ is identical with the spectrum of $Ni(TRI)(NO_3)_2 \cdot H_2O$ except for the absence from the spectrum of $Ni(TRI)_2(NO_3)_2 \cdot H_2O$ of bands which have been attributed to coordinated nitrate.[2] The same material can be formed by reaction of $Ni(TRI)(NO_3)_2 \cdot H_2O$ with 1 mole of the quinazoline.

This compound has a magnetic moment of 2.94 BM, which is consistent with the presence of a pseudo-octahedral environment about the nickel(II). This interesting chelate sandwich compound (structure III) offers an excellent example of strong trigonal distortion from O_h symmetry.



III

Absorption spectra (methanol and Nujol mull) were measured from 7400 to 33,000 cm^{-1}. Bands occur at ν_1 11,300 cm^{-1} (sh) (ϵ 1.1), ν_2 14,500 cm^{-1} (ϵ 18.7), ν_3 20,200 cm^{-1} (ϵ 212). The relatively intense color may be attributed to low-energy charge-transfer bands. The absorption bands have been assigned to the following transitions in D_{3d} symmetry: ν_1, $^3A_{2g} \rightarrow {}^3A_{1g}$; ν_2, $^3A_{2g} \rightarrow {}^3E_g$; ν_3, $^3A_{2g} \rightarrow {}^3A_{2g}$, ^3E_g (plus charge transfer). A *Dq* value of 1340 cm^{-1} for the Schiff base chelate has been calculated assuming it to be the weighed average of ν_1 and ν_2. This agrees quite well with the *Dq* value of 1320 cm^{-1} which is obtained by applying the rule of average environment[7] to the aqueous solution spectrum of $[Ni(TRI)(H_2O)_3]^{2+}$.

Two geometric isomers can be envisioned for this complex based on the relative clockwise or counterclockwise progression of the repeating unit in each Schiff base chelate ring. The two isomers would be a *meso* form, in which the repeating unit progresses in opposite directions on each Schiff base chelate ring, and a *racemic* form, in which the repeating unit progresses in the same direction. From a study of the Dreiding stereomodels, the *racemic* form appears to be improbable in that the nonbonded distance between benzene rings would be 2.8 A. The minimum distance between the benzene rings in [2.2′]paracyclophane is 2.83 A.[8,9] Differences in the ultraviolet spectra of [2.2′]paracyclophane and certain model compounds have indicated considerable interaction between benzene rings in this system.[10,11] The ultraviolet spectra of $Ni(TRI)^{2+}$ and $Ni(TRI)_2^{2+}$ in methanol are practically identical; therefore, it appears that little or no interaction exists between benzene rings. In the *meso* form, the nonbonded distance between benzene rings is approximately 3.5 A. Consequently, no interaction is expected and the compound in question is of this structure.

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Single-Crystal Preparation of Cubic Rare Earth Tungsten Bronzes

Sir:

The crystal growth of rare earth tungsten bronzes[1] by electrolytic reduction of a fused mixture of rare earth tungstate and tungsten trioxide is possible. The process is, however, complicated by the necessity to operate at relatively high temperatures. Suitable mixtures of rare earth tungstate and tungsten trioxide were found to melt between 1000 and 1200°. These temperatures are considerably higher than those employed for the well-developed technique of growing alkali tungsten bronzes or alkali molybdenum bronzes (around 600°). Several modifications on established crystal-growing methods of bronzes[2–5] were necessary in order to overcome the difficulties of an electrolysis around 1200°. Optimum conditions were determined empirically and represent numerous compromises. Major difficulties were the following: tungsten trioxide sublimes increasingly above 800°, thus changing continuously the composition of the melt; ceramic tubes, recommended to insulate the lead wire of the cathode from the melt,[3] become conducting (it was, for example, observed that little crystals grew on a shielding Degussite tubing). At 1200°, the temperature gradient can be severe, and isotherm profiles in the crystals are difficult to control. Container materials for the highly aggressive melt are hard to find.

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To prevent a severe change of the melt composition because of the continuous loss of WO_3, the crystals were grown relatively quickly from large quantities of fused earth tungstate and tungsten trioxide. It appears that the current density has to be increased when the temperature of the melt is increased. Best results were obtained by electrolyzing appropriate mixtures of tungsten trioxide and rare earth tungstate around 1200° using current densities up to 60 ma/cm^2. The crystals were grown in the thermoconstant portion of a tubular furnace which was continuously flushed with argon. The electrodes were made of platinum which was observed to have more favorable properties than nichrome, tungsten, or carbon. Recrystallized alumina (no platinum!) served as crucible material. Both single cell and double cell assemblies were used.

Instead of melting the mixture of rare earth tungstate and tungsten trioxide directly, it was found to be more advantageous to melt a mixture of rare earth chloride and tungsten trioxide.[6] The following reaction takes place

$$2RCl_3 + 6WO_3 \longrightarrow R_2(WO_4)_3 + 3WO_2Cl_2\uparrow$$

Very homogeneous melts were obtained this way. The electrolysis was usually started after the WO_2Cl_2 liberation was terminated.

Crystals grown in the course of this investigation had the composition $Sm_{0.09}WO_3$, $Gd_{0.19}WO_3$, and $Tm_{0.10}WO_3$. $Sm_{0.09}WO_3$ crystals up to 5 mm in length were obtained within 20 min at 1300° using a mixture of $SmCl_3$ and WO_3 (molar ratio 1:3). The $Gd_{0.19}WO_3$ crystals, up to 10 mm in length, were grown from a molten mixture of $GdCl_3$ and WO_3 (molar ratio 1:2) 20° above the melting point of the mixture. It may be mentioned that the gadolinium content of the $Gd_{0.19}WO_3$ crystals is somewhat higher than that of the gadolinium richest samples obtained in the form of powders by thermal reaction of Gd_2O_3, W, and WO_3.[1]

All single crystals prepared in the course of this investigation were examined by X-ray diffraction methods and analyzed for their rare earth content by magnetic susceptibility measurements.

Acknowledgments. The authors wish to thank Professor Aaron Wold of Brown University and Dr. H. Shanks of the Institute of Atomic Research, Ames Laboratory, for many stimulating discussions.

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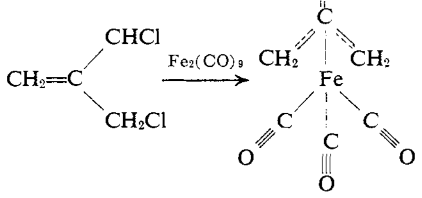
Trimethylenemethaneiron Tricarbonyl

Sir:

In many instances it has been possible to obtain transition metal π complexes containing as ligands organic molecules which in the free state are sufficiently reactive or subject to internal rearrangement to preclude their isolation under normal conditions. Some examples are the iron carbonyl complexes of cyclobutadiene,[1] benzocyclobutadiene,[1] cyclopentadienone,[2] and 2,4-cyclohexadienone.[3] We now report the isolation of a metal complex containing the organic fragment trimethylenemethane as a ligand. This hypothetical molecule has long been of theoretical interest in that it displays at its central carbon the maximum mobile bond order and minimum free valence possible for an unsaturated hydrocarbon system.[4] Its bonding to transition metals may be anticipated. Since trimethylenemethane would possess an extremely unfavorable delocalization energy, little π energy will be dissipated in donation to a metal,[5] and since theoretical treatments suggest that there is an unfilled nonbonding orbital, as with cyclobutadiene, it should also be an excellent acceptor in transition metal complexes.[6]

Excess iron enneacarbonyl was stirred with 3-chloro-(2-chloromethyl)propene (I)[7] in ether at room temperature for 12 hr; the mixture was then filtered and fractionally distilled. The pale yellow complex trimethylenemethaneiron tricarbonyl (II) was obtained in 30% yield, bp 53–55°(16 mm), mp 28.4–29.6°, $n^{30}D$ 1.5879. *Anal.* Calcd for $C_4H_6Fe(CO)_3$: C, 43.31; H, 3.12. Found: C, 43.29; H, 2.90. In the mass spectrum of II strong peaks corresponding to the parent molecular ion and fragments resulting from the successive loss of one, two, and three carbonyl groups are observed at *m/e* 194, 166, 138, and 110. This type of cracking pattern is observed with cyclobutadieneiron tricarbonyl[1] and many derivatives.[8]



I II

The infrared spectrum of the complex shows strong carbonyl absorption at 1998 and 2064 cm^{-1}, typical of symmetrical diene–$Fe(CO)_3$ complexes.[9,10] Other bands appear at 3067 (m), 3000 (m), 2885 (w), 2475 (w), 1805 (w), 1566 (w), 1478 (m), 1456 (m), 1349 (w), 1025 (w), 917 (m), and 803 cm^{-1} (m). The nmr spectrum shows a sharp singlet at τ 8.00 indicating the equivalency of all hydrogens.[11] This shift may be compared to those in the spectrum of the isomeric butadieneiron tricarbonyl in which the proton signals of the terminal positions appear at τ 8.32 (*syn*) and 9.78 (*anti*);[9,12] to the

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[11] The line width at half-height was found to be 0.6 cps. Measurements were taken on a Varian A-60.