detectable signal within reasonable data acquisition times. With our recent synthesis of the more soluble iodo analogue, we were granted an opportunity to study the solution behavior of an $Mo_2X_4(dppe)_2$ compound using $^{31}P\{^1H\}$ spectroscopy.

Several $^{31}P\{^1H\}$ spectra of β-$Mo_2I_4(dppe)_2$ recorded at different temperatures are presented in Figure 10. There is no signal at room temperature, but as one cools the solution, a broad resonance appears between −30 and −40 °C, which becomes a sharp singlet as the temperature is lowered to −80 °C (Figure 10c). The resonance is located at +14.9 ppm, which is similar to the ^{31}P chemical shift values reported for $Mo_2X_4(dppm)_2$ compounds.[18,24] In the present study, the temperature dependence of the phosphorus resonance is indicative of a low-energy fluxional process that interconverts various rotational forms of the molecule. That such a process is occurring in solution is not surprising in view of the fact that several different rotational isomers are easily stabilized in the solid state. In structure **1**, the presence of both **1a**, with a twist-chair conformation, and **1b**, which exhibits a boat conformation of the rings, suggests that the energy differences are so small that weak intermolecular packing forces become important in determining the degree of twist that the molecules assume in the crystalline state.

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Registry No. **1**, 103852-10-4; **2**, 103957-54-6; $Mo_2(O_2CCH_3)_4$, 14221-06-8; Mo, 7439-98-7.

Supplementary Material Available: Full listings of bond angles, bond distances, and anisotropic displacement parameters (9 pages); tables of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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Studies of the Photoinduced Ligand Substitution Reactions of $[Re(CNxyl)_6]^+$ (xyl = 2,6-Dimethylphenyl) in the Presence of Halide Ions

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Irradiation of $[Re(CNxyl)_6]^+$ with UV light at 20 °C in dichloromethane and in the presence of halide ions yields complexes of the type $Re(CNxyl)_5X$, where X = Cl, Br, or I. The quantum yields are quite respectable, $\phi_P = 0.2$–0.3, and isolated product yields are in the range of 30–40%. The photoproducts have been characterized by spectroscopic methods and, in the case of the new derivatives $Re(CNxyl)_5Cl$ and $Re(CNxyl)_5Br$, by elemental microanalyses. The magnitudes of the quantum yields suggest that ligand substitution occurs by a dissociative mechanism involving a reactive d–d excited state.

Introduction

While isocyanide ligands are similar to carbon monoxide in that they may serve as σ donors and/or π acids,[1,2] available evidence suggests that isocyanides are better σ donors. Thus, there are several examples of isocyanide-containing complexes of metal ions in relatively high oxidation states, e.g., $[Cr(CNR)_7]^{2+}$,[3] $[Cr(CNR)_6]^{3+}$,[4] $[Mn(CNR)_6]^{2+}$,[5] and $[Mo(CNR)_7]^{2+}$ [6,7] (R = alkyl and/or aryl), for which the isoelectronic carbonyl analogues are unknown. This means that a wider range of oxidation states can often be investigated for the isocyanide systems. In addition, the isocyanide function is versatile because the presence of the R group attached to nitrogen allows one to vary steric and electronic properties of the ligand very easily.

As photochemical methods have proved very useful in the synthesis of carbonyl complexes,[8,9] for example, in the synthesis of $Fe_2(CO)_9$,[10] they may be of importance in the preparation of isocyanide complexes as well, especially for those species that are not easily made by other routes.[11] As a case in point, we describe herein the photochemical generation of the complexes $Re(CNxyl)_5X$, where xylNC = 2,6-dimethylphenyl isocyanide and X is Cl, Br, or I. While Treichel and co-workers have reported a low-yield thermal route to the analogous $Re(CN$-p-$tol)_5X$ (X = Cl or Br) compounds by combining $Re(CO)_5X$ with p-tolyl isocyanide in refluxing toluene[12] and Cameron et al.[13] have shown that the iodo complex $Re(CNxyl)_5I$ can be prepared from K_2ReI_6, the most logical synthetic pathway is via the readily available homoleptic isocyanide cations $[Re(CNR)_6]^+$.[14,15] However, these 18-electron species are kinetically inert to ligand substitution reactions under thermal conditions, and some means of activation is therefore necessary. As shown below, photoinduced substitution of a xylyl isocyanide ligand of $[Re(CNxyl)_6]PF_6$ proceeds very cleanly in CH_2Cl_2, and the quantum efficiencies are rather high, $\phi_P \sim 0.2$.

Experimental Section

Starting Materials. $(n\text{-}Bu_4N)_2Re_2Cl_8$ was prepared by the method of Barder and Walton[16] and converted into $Re_2(O_2CCH_3)_4Cl_2$ according to the standard literature procedure[17] with a single important modification. The orange precipitate of $Re_2(O_2CCH_3)_4Cl_2$, which is formed after refluxing $(n\text{-}Bu_4N)_2Re_2Cl_8$ in CH_3COOH/acetic anhydride for 2 h, was too fine to be filtered conveniently and so had to be centrifuged, the supernatant decanted, and the solid washed successively with EtOH and Et_2O several times, centrifuging between each wash. The yield of product was 82%. The method of Cameron et al.[15] was used to prepare $[Re(CNxyl)_6]PF_6$ from $Re_2(O_2CCH_3)_4Cl_2$ with only minor changes as follows. Twenty milliliters of MeOH was added to a flask containing 0.48

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Table I. Physical Data and Quantum Yields

complex	λ_{max},[a] nm	ϵ_{max}, M^{-1} cm^{-1}	$\nu(C{\equiv}N)$,[b] cm^{-1}	ϕ_P	λ_{irr}, nm	$E_{1/2}$,[c] V vs. AgCl/Ag
$[Re(CNxyl)_6]^+$	300	95100	2067 s[d]			
	330 sh	56000	1998 m[d]			
	350 sh	45000				
$Re(CNxyl)_5Cl$	322	70900	2041 s	0.30 (2)	319	0.49
	390 sh	16700	2000 m			1.44[e]
	435 sh	7400	1950 sh			
			1902 m			
$Re(CNxyl)_5Br$	322	68000	2051 s	0.24 (2)	319	0.48
	390 sh	12900	2006 m			1.40[e]
	430 sh	6000	1964 m			
			1906 m			
$Re(CNxyl)_5I$	322	63400	2049 s	0.23 (2)	321	0.47
	385 sh	16500	2006 m			1.40[e]
	420 sh	5100	1963 m			
			1906 m			

[a] CH_2Cl_2 solution at 20 °C. [b] Nujol mull infrared spectra. [c] Pt-based working electrode in 0.1 M TBAH–CH_2Cl_2 solution. [d] Data taken from ref 15. [e] $E_{p,a}$ value of an irreversible process for which $i_{p,a}/i_{p,c} >> 1$.

g of $Re_2(O_2CCH_3)_4Cl_2$ and 3.0 g of xylyl isocyanide, and the suspension was stirred under reflux for 2 days. The mixture turned a deep purple and remained that color for a full day before turning the expected brown color. After 2 days, the brown mixture was cooled to room temperature and the solvent evaporated under a stream of gaseous N_2. A quantity of KPF_6 (0.4 g) dissolved in 40 mL of acetone was added to the brown residue and this mixture was stirred for 30 min. The resulting solution was reduced to dryness, and the product, $[Re(CNxyl)_6]PF_6$, was extracted into CH_2Cl_2 and precipitated out with petroleum ether. The white solid was filtered off, washed with petroleum ether, and dried in vacuo. The product was recrystallized once from CH_2Cl_2/petroleum ether and twice from acetone/diethyl ether; yield 64%.

The halide salts, *n*-Bu_4NBr, *n*-Bu_4NI, and $[(PhCH_2)(Et)_3N]Cl$, were all obtained from Aldrich Chemical Co. Xylyl isocyanide was purchased from Fluka AG. The dichloromethane used in the quantum yield studies was from Burdick and Jackson (Distilled in Glass); that used in the photosynthetic irradiations was from Baker Chemical Co. (Photorex grade). The ethanol and ether solvents used in the recrystallizations of the products were reagent grade.

Instrumentation and Physical Measurements. The UV–vis spectral studies were carried out on a Cary 17D spectrophotometer. The quantum yields were measured with an Oriel 1000-W xenon arc lamp in line with an Oriel 7241 monochromator. Infrared spectral measurements were made with an IBM IR/32 Fourier transform spectrometer. Mass spectral data were obtained with a Finnigan 4000 GC/MS by a chemical ionization method. Electrochemical measurements were carried out with a Pt-bead working electrode in dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Procedural Methods. The study was conducted in three parts: (1) measurement of quantum yields, (2) synthesis and purification of the three halide photoproducts, and (3) the characterization of the photoproducts.

For the quantum yield studies, a stock solution of $[Re(CNxyl)_6]^+$ in CH_2Cl_2 was prepared. Typically, the concentration was 3.00×10^{-5} M and the absorbance at 300 nm was 2.85. Four-milliliter aliquots were placed in three quartz freeze–pump–thaw cells that contained small magnetic stirbars (7 × 2 mm). To these solutions were added 10-equiv samples of the appropriate halide salts. The cells were then degassed and charged with nitrogen. During irradiation the samples were stirred magnetically. Quantum yields were obtained from plots of integrated rate expression[18]

$$-\frac{C_T V}{I_0}[\ln (C_T - C_P) - \ln (C_T)](1 - 10^{-A_T}) = \phi_P t \qquad (1)$$

where C_T is the total concentration of rhenium in the sample, V is the photolyte volume, I_0 is the light flux in einsteins per second, C_P is the concentration of photoproduct at time t, and A_T is the total absorbance at the wavelength irradiated.

This expression is valid if the product is formed from $[Re(CNxyl)_6]^+$ with 1:1 stoichiometry and the wavelength irradiated corresponds to an isosbestic point.[18] The latter condition was satisfied when the Br^-- and Cl^--containing samples were irradiated at 319 nm and the I^--containing sample was irradiated at 321 nm. We have also assumed that the light absorbed by the photoproduct does not affect the yield, either by induction of the back-reaction or by sensitization of the reaction of interest. Since the spectra of the reactant and product overlapped, the quantity C_P was determined by solving simultaneously for the absorbances at two wavelengths. The light flux was measured with the ferrioxalate actinometer.[19]

When the isolation of photoproduct was desired, the reagent solution was prepared by adding 100 mg of $[Re(CNxyl)_6]PF_6$ to 300 mL of deoxygenated dichloromethane. Five equivalents of the halide salt was added, and this solution was irradiated for ~6–8 h with a low-pressure mercury-vapor arc lamp. A Pyrex sheath was used on the lamp since uncharacterized (possibly ligand-based) photochemistry took place if wavelengths shorter than 300 nm were employed. The solvent was then removed by rotary evaporation, and the product was purified by successive recrystallizations from ethanol and finally ether.

Results

Photolyses. Independent of the halide ion used, photolysis proceeded smoothly and multiple isosbestic points were observed. Figure 1 shows the spectral changes observed on the low-energy side of the absorption spectrum of $[Re(CNxyl)_6]^+$ when it was irradiated at 319 nm in CH_2Cl_2 in the presence of chloride. Note that isosbestic points were maintained at 319, 340, and 362 nm until photolysis was essentially complete. Thus, secondary photolysis reactions posed no real problems, and to all intents and purposes a single rhenium-containing photoproduct was obtained in each case. However, slight deviations from the behavior predicted by eq 1 were sometimes observed when the primary photoreaction was nearly complete, perhaps because a minor secondary photoreaction became significant. Quantum yields, calculated according to eq 1, are given in Table I. Isolated yields were 32%, 35%, and 40%, respectively, for the chloride, bromide, and iodide derivatives.

Product Characterization. Comparison with the absorption spectrum of an authentic sample showed that the photoproduct obtained from the iodide-containing solution was $Re(CNxyl)_5I$. Elemental microanalyses of the photoproducts revealed that the corresponding halides $Re(CNxyl)_5Cl$ and $Re(CNxyl)_5Br$ were formed upon irradiation in the presence of chloride and bromide ions, respectively. Anal. Calcd for $C_{45}H_{45}ClN_5Re$: C, 61.53; H, 5.17. Found: C, 61.66; H, 5.43. Calcd for $C_{45}H_{45}BrN_5Re$: C, 58.62; H, 4.92. Found: C, 57.31; H, 5.16. As a further check, the mass spectrum of the bromide-containing photoproduct was

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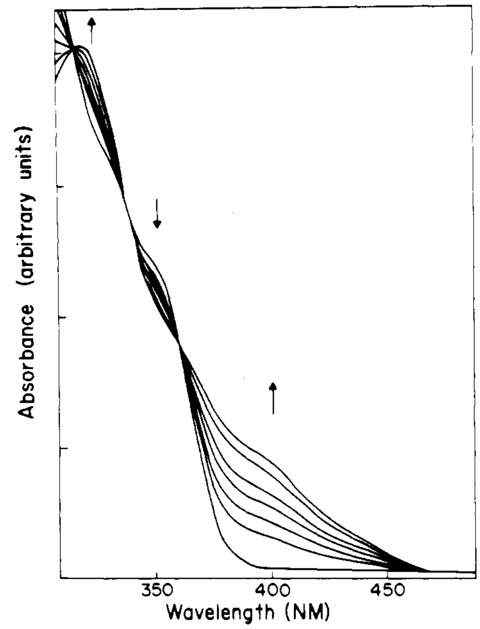

Figure 1. Absorption spectra of a CH_2Cl_2 solution containing $[Re(CNxyl)_6]^+$ and a source of chloride ion. The arrows indicate the direction of the absorbance changes after successive irradiations at 319 nm and 20 °C.

recorded; the parent ion peak corresponded to $Re(CNxyl)_5Br$. In addition to the analytical data, the infrared spectral results in the C≡N stretching region confirm the identities of the photoproducts. The bands observed in the IR spectra as well as the UV–visible spectra of the various derivatives are compiled in Table I.

The cyclic voltammetric data for these three complexes are also summarized in Table I. All three products showed two redox processes that differed only slightly as the halogen varied from chloride to bromide to iodide. Both processes could be assigned to oxidations and are attributed, in the order of increasing potential, to the $[Re(CNxyl)_5X]^{+/0}$ and $[Re(CNxyl)_5X]^{2+/+}$ couples, respectively, where X denotes a halogen. For each sample the latter couple is irreversible; only the anodic wave is observed.

Discussion

Identification and Characterization of Photoproducts. For each halide, X = Cl, Br, or I, the photoproduct is unambiguously identified as the mixed-ligand complex $Re(CNxyl)_5X$. Chemical analyses and spectral comparison support the product formulations. In particular, all three products exhibit very similar IR spectra, especially in the C≡N stretching region (Table I). Although the products are undoubtedly pseudooctahedral, the effective symmetry must be lower than C_{4v} since it permits only three dipole-allowed C≡N stretching vibrations. This presumably reflects a nonlinearity in some (or all) of the Re—C≡N—C units, a result that accords with spectroscopic data for other isocyanide complexes of rhenium.[20] In lower symmetries all five C≡N stretching vibrations are likely to be dipole-allowed. Since only four bands are resolved, we conclude that there is an accidental degeneracy or that one of the transitions is simply too weak to be observed. Selected totally symmetric streching vibrations have been found to be quite weak in related systems.[21]

The electronic absorption spectral properties of the products are also consistent with the proposed structures. As discussed below, the intense transitions observed in the UV–visible spectra of $[Re(CNxyl)_6]^+$ and the photoproducts can be attributed to metal-to-ligand charge-transfer (MLCT) transitions. As expected, these transitions undergo a distinct bathochromic shift when a halide ligand is introduced into the coordination sphere of rhenium. The shifts can be attributed, in large part, to charge-induced stabilization of the Re(II) moiety that is created, at least in a formal sense, during the MLCT process.

A similar stabilization of the Re(II) state is apparent from the electrochemical results. Previously, Cameron et al. reported that $[Re(CNxyl)_6]^+$ exhibited an oxidation at +1.19 V vs. SCE.[15] The wave at ~0.5 V observed for $Re(CNxyl)_5I$ was tentatively ascribed to a redox process occurring at the coordinated iodide;[13] however, the occurrence of similar waves in the voltammograms of the chloride and bromide derivatives strongly argues that the redox process is metal-based. We believe that this can be attributed to the $[Re(CNxyl)_5X]^{+/0}$ couple, which is shifted by ~0.7 V to more negative potentials relative to that for $[Re(CNxyl)_6]^{2+/+}$. The next oxidation step should be more accessible as well; hence, the process at $E_{p,a} \sim +1.4$ V can be assigned to the metal-based oxidation $[Re(CNxyl)_5X]^+ \rightarrow [Re(CNxyl)_5X]^{2+} + e^-$. These data agree exceedingly well with the only previous report on the redox chemistry of species of the type $Re(CNR)_5X$; cyclic voltammetric data for CH_2Cl_2 solutions of $Re(CN\text{-}p\text{-}tol)_5X$ (X = Cl or Br) show $E_{1/2} = +0.5$ V and $E_{p,a} \sim 1.3$ V vs. SCE.[12] The absence of a wave corresponding to the reduction of $[Re(CNxyl)_5X]^{2+}$ is most likely a consequence of the rapid decomposition of this 16-electron species. The stabilization of rhenium(III) isocyanide complexes apparently requires the presence of more halide ligands than are encountered in the case of $[Re(CNxyl)_5X]^{2+}$ and/or seven-coordination.[14,15]

Evaluation of Method and Mechanistic Considerations. As long as the irradiation wavelength was above 300 nm, the photolyses were very clean and led to a single photoproduct in each case. The quantum yields are quite reasonable, so that the times required for irradiation were not excessive. The isolated yields are modest, but this was due to the difficulties encountered in separating the $Re(CNxyl)_5X$ species from the electrolyte introduced as a halide source. Presumably, larger yields could have been achieved if the halide salts $[Re(CNxyl)_6]X$ had been isolated and used as starting materials. In any case the photolytic procedure has been established as a viable synthetic method.

Although a detailed mechanistic analysis is beyond the scope of this study, some consideration of mechanistic alternatives is worthwhile since it is relevant to the formulation of synthetic strategies for related systems. The two limiting mechanisms for ligand substitution processes are the dissociative and the associative pathways. As discussed below, either is possible for the systems under investigation, but the quantum efficiencies are more consistent with a dissociative pathway.

Photoinduced dissociation of a carbon monoxide ligand is a well-established process in metal carbonyls. This process is favored by the bond weakening that occurs on formation of a metal-centered excited state wherein a $d\pi$ electron is excited into a $d\sigma^*$ orbital.[9] Ligand ejection can be a very rapid process;[22] hence, high quantum yields are obtainable. Although the associative pathway is less commonly observed in photoinduced substitution processes, there are systems for which steric[11] and electronic[23] evidence points to an associative pathway. Metal-to-ligand charge-transfer excited states are prone to this type of reaction because an orbital vacancy and increased positive charge are created at the metal center as a result of the excitation process.[24]

The electronic absorption spectrum of $[Re(CNxyl)_6]^+$ exhibits several very intense absorption bands in the UV region analogous to those of $M(CNPh)_6$ complexes where M is a group 6 metal. In these systems the transitions have been assigned as metal-to-ligand charge-transfer bands.[11,25] Similar assignments are proposed for the Re(I) system. Hence, we must consider the possibility that the photochemistry occurs by an associative reaction of a charge-transfer excited state. Although the associative process

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is inherently a bimolecular one, in our studies the reactants are expected to be strongly ion-paired, and the efficiencies need not be limited by diffusional processes.[26] Consistent with an associative mechanism, there is a slightly positive correlation between the yields and the nucleophilicities of the halogens in Table I; however, this may reflect relative ion-pairing efficiencies that have not been measured.

More to the point, the quantum yields appear to be incompatible with an associative mechanism as they are much larger than those that have been found in previous studies where associative substitution reactions have been implicated.[11,23] In general, substitution yields are expected to be relatively small for associative processes. In the first place the addition of another ligand is likely to be disfavored by ligand–ligand repulsion effects, especially for systems with a coordination number of 6 or higher. In contrast, the same repulsions would favor ligand expulsion by a dissociative process. Secondly, in the transition state of an associative process there is inevitably a partitioning between two modes of deactivation: return to the initial state and conversion to product.

In view of the quantum yields we have observed, we tentatively ascribe the reaction to a dissociative mechanism, presumably originating from a reactive d–d excited state. No d–d excited states have been identified in the absorption spectrum of $[Re(CNxyl)_6]^+$, but they could be masked by the charge-transfer absorptions, which have much greater oscillator strengths. If the d–d state is not the lowest energy excited state, it is sufficiently low-lying that it can be thermally populated.

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Registry No. $Re(CNxyl)_6^+$, 87829-86-5; $Re(CNxyl)_5Cl$, 103904-91-2; $Re(CNxyl)_5Br$, 103904-92-3; $Re(CNxyl)_5I$, 103904-93-4.

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Magnetic Studies of a Linear Chromium(III) Trimer of a Triketone

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The trinuclear chromium(III) triketonate complex, $Cr_3(lig)_2$, where lig = 1,5-diphenyl-1,3,5-pentanetrionato, has been synthesized and characterized by magnetic susceptibility, ESR, and electronic spectra. The complex has $g = 1.977$ and exhibits antiferromagnetic interactions. The magnetic interaction fits an isosceles arrangement of the coupling constants, with $J = -6.00$ cm^{-1} between two pairs of adjacent metal atoms and $J' = -1.35$ cm^{-1} between the third metal pair. This arrangement is compatible with the essentially linear configuration of the metal atoms also expected with the planar ligands.

Introduction

In the past two decades the number of polynuclear complexes of transition metals reported has increased dramatically. Several dimeric chromium(III) complexes have been thoroughly investigated structurally and magnetically,[1] but few trinuclear chromium complexes have been reported. Trinuclear basic carboxylate complexes were studied by various methods. Crystal structures indicate that the three atoms are essentially an equilateral triangle surrounding a central oxygen atom.[2] They have been investigated magnetically[3–6] and were the first compounds in which exchange interactions between the metals were suggested.[3] Although incorrect expressions were occasionally used,[5] a Heisenberg spin-coupling Hamiltonian was shown to give general agreement between magnetic and strutural data. However, a slightly isosceles configuration of the magnetic coupling parameters gives the best agreement, despite the equilateral structural arrangement; moreover, slightly different parameters were required for ESR and specific heat data. Introduction of coupling between adjacent trinuclear molecules gives better agreement.[7–9] Newer basic carboxylates continue to be reported.[10] Recently, Blake and co-workers[11] have also reported magnetic properties of heterotrinuclear basic acetates of Cr(III) with divalent metal ions.

There are few other reports of trinuclear complex formation. Stunzi and Marty[12] report the hydrolytic polymers formed upon addition of OH^- to $[Cr(H_2O)_6]^{3+}$. Connick et al.[13] also report hydrolytic polymerization of Cr(III) and suggest a trinuclear complex on the basis of the magnetic data. However, the essentially constant magnetic moment, between 329 and 274 °C, gives no information on magnetic coupling or on structure. A similar problem voids any structural information from the magnetism of binuclear analogues.[14] Karayannis et al.[15] report the preparation of chromium complexes with purine bases, $Cr_3L_5Cl_4{\cdot}2H_2O$ (purine or adenine) as possible models for DNA–RNA interaction with Cr(III). Despite the trinuclear empirical formula, the complexes are presumed to be infinite polymers,[15] though no structural or magnetic information is available.

We report here the preparation and properties of the first linear trinuclear chromium complex using the ligand 1,5-diphenyl-1,3,5-pentanetrione.

Experimental Section

Synthesis of $Cr_3(C_{17}H_{12}O_3)_2(C_2H_5OH)_2(H_2O)(OH)_5$ and $Cr_3(C_{17}H_{12}O_3)_2(H_2O)_3(OH)_5$. One gram (3.75 mmol) of 1,5-diphenyl-1,3,5-pentanetrione was refluxed in 25 mL of ethanol in a 250-mL RB flask for 20 min. Urea (8.86 g, 0.148 mol), dissolved in 50 mL of a 1:1 mixture

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