

was used to test for possible silicon incorporation in  $\text{ErN}_{1-x}$  synthesized from  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Er}$  contaminated with  $\sim 2$  mol %  $\text{LiN}(\text{SiMe}_3)_2$ ; an upper limit of Si as 1 wt % was found. The silicon content of  $\text{Er}_2\text{O}_3$  (Aldrich 99.9%) used to prepare  $\text{ErCl}_3$  is less than 15 ppm, and thus trace Si incorporation is possible. Mass balance supported the contention that the ammonolysis of  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Ln}$  proceeded smoothly, as indicated by the calculated and observed weight losses in Table I.

A distinct advantage to the melt technique concerns the ready preparation of  $\text{Ln}_{1-y}\text{Ln}'_y\text{N}_{1-x}$  solid solutions, provided the constituents possess compatible ionic radii. Following the standard procedure,<sup>20</sup> a melt containing a 1:1 ratio of  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Y}$  and  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Sm}$  in addition to traces of LiCl (vide infra)<sup>21</sup> led to  $\text{Y}_{0.5}\text{Sm}_{0.5}\text{N}_{1-x}$  after annealing at 600 °C for 24 h. The diffraction lines (found:  $a = 4.968$  (3) Å) of the mixed lanthanide compound are broad and between those of the binary compounds (average of literature<sup>23</sup> values:  $a = 4.971$  Å), indicative of a solid solution (see supplemental Figure 1).<sup>11,27</sup>

**Onset of Crystallization.** When higher purity  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Ln}$  ( $\text{Ln} = \text{Y}, \text{La}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Yb}$ ;  $<0.5\%$   $\text{LiN}(\text{SiMe}_3)_2$ ) was utilized in Scheme I, an annealing temperature of 850 °C (24 h) was required to provide  $\text{LnN}_{1-x}$ . However, if 1–3 mol %  $\text{LiN}(\text{SiMe}_3)_2$  was present in  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Ln}$  ( $\text{Ln} = \text{Pr}, \text{Nd}, \text{Er}$ ) or when 10–15 mol % was ground and melted together with higher purity  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Yb}$ , crystalline  $\text{LnN}_{1-x}$  formed upon annealing for 24 h at 575 °C. Rapid ammonolysis of  $\text{LiN}(\text{SiMe}_3)_2$  must occur, and the resulting  $\text{LiNH}_2$  (tetragonal,  $I4$ ,  $a = 5.016$  Å,  $c = 10.22$  Å)<sup>28</sup> catalyzes the crystallization of  $\text{LnN}_{1-x}$ . Transport processes mediated by protons or lithium from trace  $\text{LiNH}_2$  (i.e., mineralization)<sup>29</sup> may increase nitrogen diffusion.

Lower annealing temperatures (Scheme I, 475 °C, 24 h) were also evident for  $\text{LnN}_{1-x}$  ( $\text{Ln} = \text{Y}, \text{Sm}, \text{Yb}$ ) when adventitious LiCl was present.<sup>21</sup> In a control experiment, LiCl (10–15 mol %,  $Fm3m$ ,  $a = 5.1396$  Å)<sup>23</sup> was ground together with the higher purity  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Yb}$ . Evidence for crystalline  $\text{YbN}_{1-x}$  ( $t \sim 40$ – $50$  Å) was obtained at 200 °C, and the material crystallized ( $t \sim 100$  Å) upon annealing at 475 °C for 24 h. A mineralization process is again viewed as responsible for the lower onset of crystallization, although LiCl (mp 614 °C) may be capable of serving as a flux.

Since both LiCl and  $\text{LiNH}_2$  possess lattice parameters near those of the lanthanide nitrides, a mechanism whereby the impurities seed the crystallization of  $\text{LnN}_{1-x}$  was considered. However, when  $\text{YN}_{1-x}$  ( $a = 4.895$  (1) Å), prepared using the high temperature method of Klemm (i.e.,  $\text{Y} + \text{NH}_3$  at 950 °C),<sup>12</sup> was added (15 mol %) to the high-purity  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Ln}$  ( $\text{Ln} = \text{Y}, \text{Sm}$ ;  $<0.5\%$   $\text{LiN}(\text{SiMe}_3)_2$ ) precursors, crystallization occurred near 850 °C (24 h). Since  $\text{YN}_{1-x}$  did not seed the formation of  $\text{YN}_{1-x}$  or  $\text{SmN}_{1-x}$ , mineralization mechanisms are considered the most likely explanation for the aforementioned catalyses.

**$\text{LnN}_{1-x}$  Properties.** The colors of the lanthanide nitrides prepared via the melt technique (Table I) may indicate that their physical properties deviate from those of conventionally synthesized black powders. Unfortunately, attempts to measure accurate conductivities have been hampered by difficulties in producing clean pellets, presumably due to surface oxide impurities. Variable-temperature magnetic susceptibility measurements of  $\text{PrN}_{1-x}$  revealed paramagnetic behavior to 4.2 K, with an ambient temperature magnetic moment of 3.5  $\mu_B$ , a value similar to that previously reported for  $\text{PrN}_{1-x}$  prepared via high-temperature methods.<sup>30</sup> No magnetic ordering was observed, although such phenomena have been postulated for truly stoichiometric  $\text{LnN}_{1-x}$ .<sup>31</sup> It is proposed that fewer nitrogen deficiencies are present in the melt-prepared  $\text{LnN}_{1-x}$  due to lower annealing temperatures, yet

the presence of interstitial hydrides,<sup>32</sup> amides, or imides may be the origin of some differences in physical properties, since  $\text{NH}_3$  is used in the synthesis. Lanthanide vacancies may also play a role. Methods to detect hydrogen, such as elastic recoil spectrometry,<sup>33</sup> have not yet been attempted.

The molten molecular precursor technique is currently being extended to ternary systems, and mechanistic studies pertaining to the catalysis of the onset of crystallization are continuing.

**Acknowledgment.** Support from the Air Force Office of Scientific Research (Grant AFOSR-87-0103) and the Cornell Materials Science Center (National Science Foundation) is gratefully acknowledged. We thank Dr. Mark M. Banaszak Holl, Prof. Francis J. DiSalvo, Dr. Patrick Lambert, and Prof. Robert McCauley for helpful suggestions and Scott Elder, Michael Rutzke, Steve Trail, and John Hunt for experimental assistance.

**Supplementary Material Available:** XRD patterns for  $\text{Y}_{0.5}\text{Sm}_{0.5}\text{N}_{1-x}$ ,  $\text{YN}_{1-x}$ , and  $\text{SmN}_{1-x}$  prepared from a melt containing a 1:1 ratio of  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Y}$  and  $\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Sm}$  in addition to traces of LiCl (Figure 1) (1 page). Ordering information is given on any current masthead page.

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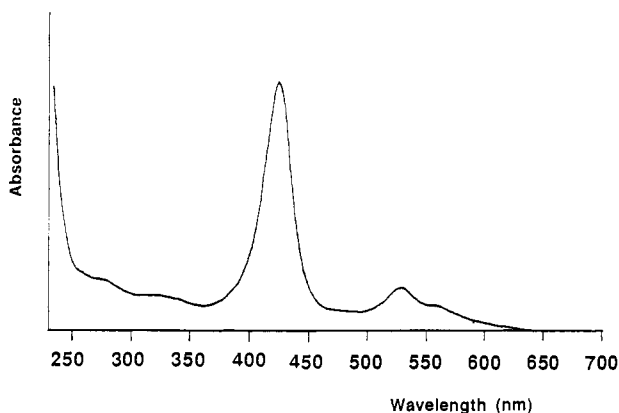
Received October 25, 1991

### Isolation and Characterization of a (Diphenylamido)ruthenium(IV) Porphyrin

Transition-metal dialkylamides are of considerable importance possibly due to their stabilization of unusual coordination numbers and valence states of metal ions, their interesting reactivity, and their possible connection to catalytic amination procedures.<sup>1</sup> Our interest in the (dialkylamido)ruthenium complexes was inspired by the following considerations. Several types of ruthenium(IV) porphyrins have been reported, including dinuclear ( $\mu$ -oxo);<sup>2</sup> dihalogeno-;<sup>3</sup> dialkyl-;<sup>3–5</sup> monooxo-;<sup>6</sup> and monomeric dialkoxy-ruthenium(IV)<sup>7</sup> porphyrin complexes. Since the dialkylamido

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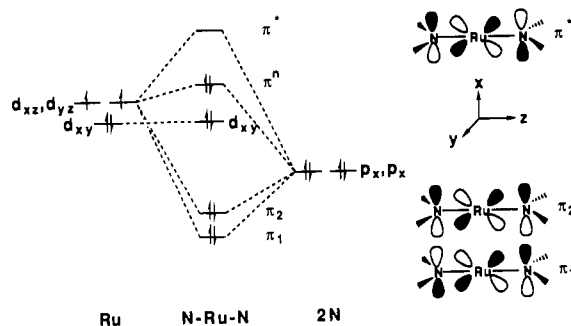


**Figure 1.** UV-visible spectrum of Ru(3,4,5-MeO-TPP)(NPh<sub>2</sub>)<sub>2</sub> (**3**) (CHCl<sub>3</sub>).

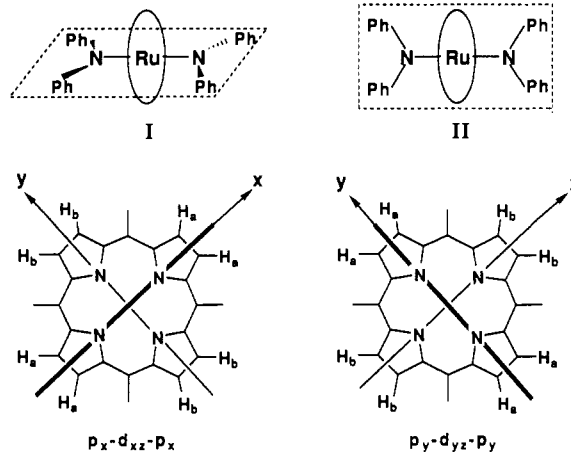
ligand NR<sub>2</sub> acts as both a two-electron  $\sigma$  donor and a two-electron  $\pi$  donor,<sup>1,8</sup> it should also form a strong bond with the Ru(IV) ion, which has vacant d orbitals. This communication reports the synthesis and spectroscopic characterization of the first (dialkylamido)ruthenium porphyrin.

Oxidation of carbonyl (*meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato)ruthenium(II) [Ru(3,4,5-MeO-TPP)(CO) (**1**)]<sup>9</sup> with 3-chloroperoxybenzoic acid (*m*-CPBA) in dichloromethane yielded a dioxoruthenium(VI) porphyrin, [Ru(3,4,5-MeO-TPP)(O)<sub>2</sub> (**2**)].<sup>10</sup> Treatment of **2** with diphenylamine in dichloromethane afforded the bis(diphenylamido)ruthenium(IV) complex Ru(3,4,5-MeO-TPP)(NPh<sub>2</sub>)<sub>2</sub> (**3**). **3** could be purified by chromatography on Al<sub>2</sub>O<sub>3</sub> column using dichloromethane as the eluent. Recrystallization of **3** from dichloromethane–heptane yielded dark purple crystals (yield: 65%). A satisfactory elemental analysis has been obtained for **3**.<sup>11</sup>

The UV-visible spectrum<sup>12</sup> of **3** is shown in Figure 1. According to the classification scheme developed by Buchler and co-workers for electronic spectra of metalloporphyrins,<sup>13</sup> **3** basically exhibits a hypso absorption spectrum. However, the long tail to the red of the Q(0,0) band suggests possible extra underlying forbidden transitions. Therefore, the spectrum of **3** can be classified as hypso/hyper. It is noteworthy that the difference ( $\lambda_{\max}$ ) between the Soret bands of **3** and **2** or between the Q bands of **3** and **1** is very small (ca. 2 nm).<sup>9,10,12</sup> Along the series **1**  $\rightarrow$  **3**  $\rightarrow$  **2**, a systematic red shift of the Soret band and a blue shift of the Q bands were observed. Significantly, in contrast with the spectrum of **3**, all the spectra of bis(amine)ruthenium(II) porphyrins Ru(Por)(NH<sub>2</sub>R)<sub>2</sub> (Por = TPP, 3,4,5-MeO-TPP; R = Bu,<sup>14a</sup> iPr, cyclohexyl<sup>14b</sup>) and Ru(Por)(NHR)<sub>2</sub> (R = Me, Et<sup>14b</sup>)



**Figure 2.** Qualitative MO scheme showing  $\pi$  interactions between ruthenium and nitrogen atoms of **3**.



**Figure 3.** Schematic diagram showing equalization of the pyrrole protons ( $H_\beta$ ) of **3** in the room-temperature <sup>1</sup>H NMR measurements.

show the Soret bands and Q(1,0) bands at ca. 410 and 506 nm, respectively.

Complex **3** gave a well-resolved <sup>1</sup>H NMR spectrum.<sup>12</sup> The porphyrin ring resonances ( $H_\beta$ ,  $H_\alpha$ , *p*-OCH<sub>3</sub>, *m*-OCH<sub>3</sub>) are typical of those for diamagnetic species containing 3,4,5-MeO-TPP.<sup>15</sup> The phenyl proton resonances ( $H'_o$ ,  $H'_m$ ,  $H'_p$ ) of the axial amido ligands appear in a pattern similar to those observed for the bis(triphenylphosphine)bis(diphenyl thioether)ruthenium(II) porphyrins.<sup>16</sup> However, the upfield shifts due to the porphyrin ring current for these protons, especially for the ortho protons, are much larger for complex **3**. This could be expected, since the Ru–N bond in the amido ruthenium(IV) complex (**3**) should be remarkably shorter than the Ru–P and Ru–S bonds in the (triphenylphosphine)- and the (thio ether)ruthenium(II) complexes.

The diamagnetic monomeric nature of **3** seems striking, since all the isolated monomeric dialkoxoyron(IV),<sup>17</sup> -ruthenium(IV),<sup>7</sup> and -osmium(IV)<sup>18</sup> ( $d^4$ ) porphyrins and the dihalogeno-ruthenium(IV)<sup>3</sup> or -osmium(IV)<sup>18b</sup> porphyrins are paramagnetic. However, prior to our study, Collman and co-workers reported a series of diamagnetic monomeric dialkylruthenium(IV) porphyrins.<sup>4</sup> In our case, the diamagnetism of **3** could be understood by a consideration of the N–Ru  $\pi$  bonding. Considering that all the reported crystal structures of transition-metal diphenylamido complexes show planar geometry about N of the amido ligand,<sup>16,19</sup> it would be probable that the corresponding geometry in complex

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- (10) Spectroscopic data for **2** are as follows. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz,  $\delta$  referenced to TMS):  $H_\beta$  9.20 (8 H, s),  $H_\alpha$  7.61 (8 H, s), *p*-OCH<sub>3</sub> 4.21 (12 H, s), *m*-OCH<sub>3</sub> 3.99 (24 H, s); IR (Nujol):  $\nu_{Ru=O}$  821 cm<sup>-1</sup> (strong). UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  427 (Soret), 522, 548 nm.
- (11) Anal. Calcd for **3**, C<sub>80</sub>H<sub>72</sub>N<sub>6</sub>O<sub>12</sub>Ru: C, 68.12; H, 5.15; N, 5.96. Found: C, 67.99; H, 4.96; N, 5.66.
- (12) Spectroscopic data for **3** are as follows. UV/Vis (1.09  $\times$  10<sup>-5</sup> M, CHCl<sub>3</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) 425 (5.19), 529 (4.42), 559 (4.21) nm. <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>,  $\delta$  referenced to TMS):  $H_\beta$  8.37 (8 H, s),  $H_\alpha$  7.04 (8 H, s), *p*-OCH<sub>3</sub> 4.15 (12 H, s), *m*-OCH<sub>3</sub> 4.02 (24 H, s),  $^{-}N(C_6H_5)_2$   $H'_o$  2.71 (8 H, d),  $H'_m$  5.92 (8 H, tm),  $H'_p$  6.23 (4 H, tm).
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3 should also be planar. This would lead to the formation of quite strong N-Ru  $\pi$  bonds as depicted in Figure 2. Absence of electrons on the  $\pi^*$  level should stabilize this system.

Although we have been unable to perform X-ray structure determinations of 3, the eclipsed orientation of the axial diphenylamido ligands is suggested by the following lines of evidence. (i) The equivalence of the ortho protons and the equivalence of the *m*-methoxy protons or the porphyrin ring phenyl group shown in the  $^1\text{NMR}$  spectrum of 3 indicate mirror symmetry in the porphyrin plane for the solution structures. This mirror symmetry should be absent for the staggered orientation of the  $\text{NPh}_2$  groups. (ii) An eclipsed orientation of the  $\text{SPh}_2$  groups in the  $\text{Ru}^{\text{II}}(\text{OEP})(\text{SPh}_2)_2$ , which contains only a small degree of Ru-S  $\pi$  back-bonding, has even been observed by James and co-workers through X-ray crystallographic studies.<sup>16a</sup> It seems likely that complexes  $\text{Ru}(\text{OEP})(\text{SPh}_2)_2$  and 3 have similar structures, and the latter should favor this orientation to a larger extent owing to N-Ru-N  $\pi$  bonding. (iii) A staggered orientation of the two  $\text{NPh}_2$  groups would cause 3 to be paramagnetic, which is in contrast with the observed diamagnetism of 3. (iv) The singlet of the pyrrole proton resonances ( $\text{H}_\beta$ ) of 3 observed in the room-temperature  $^1\text{H}$  NMR spectrum is not incompatible with the presumed structure of  $D_{2h}$  symmetry for 3. Although  $p_x(\text{N})\text{-}d_{zz}(\text{Ru})\text{-}p_x(\text{N})$   $\pi$  bonding would lower the symmetry of the porphyrin, leading to the splitting of the pyrrolic protons into two sets ( $\text{H}_a$  and  $\text{H}_b$ ) as shown in Figure 3, we do not expect that this bonding is so strong as to prevent the rotation of diphenylamide groups. The shuttling of the molecule of 3 between the diamagnetic conformations I and II would be rapid, leading to the observation of a singlet for the pyrrole proton resonances in the  $^1\text{H}$  NMR measurements even at  $-45^\circ\text{C}$ .

In addition, the IR spectrum of 3 shows no N-H stretching bands. The "oxidation state marker" band<sup>20</sup> (sharp and strong) appears at  $1012\text{ cm}^{-1}$ , which is consistent with the +4 oxidation state of ruthenium.

3 is air-stable in the solid state. In dichloromethane solution, it exhibits no quick reaction with alcohol and triphenylphosphine. Oxidation of 3 with *m*-CPBA afforded the dioxo complex 2.

**Acknowledgment.** We acknowledge support from the University of Hong Kong and Hong Kong Research Council.

(20) Our studies on metalloporphyrins indicated that this band was very useful to the characterization of both ruthenium and osmium TPP or substituted-TPP complexes. See also: Groves, J. T.; Ahn, K.-H. *Inorg. Chem.* 1987, 26, 3831. The "oxidation state marker" bands of 1 and 2 are  $1007$  and  $1019\text{ cm}^{-1}$ , respectively. The bis(amine)ruthenium(II) porphyrins  $\text{Ru}(\text{Por})(\text{NHR}_2)_2$  and  $\text{Ru}(\text{Por})(\text{NHR}_2)_2$  (see text) show the "oxidation state marker" bands ranging from  $998$  to  $1004\text{ cm}^{-1}$ .

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Received September 9, 1991

### Syntheses and X-ray Structures of Novel Phenoxo-Bridged Binuclear Complexes: Bis( $\mu$ -phenoxo)bis[bis(acetylacetonato)chromium(III)] and Its Para-Substituted Phenoxo Analogues

In contrast to a relatively large number of hydroxo- or alkoxo-bridged binuclear complexes,<sup>1-5</sup> there have been only a very

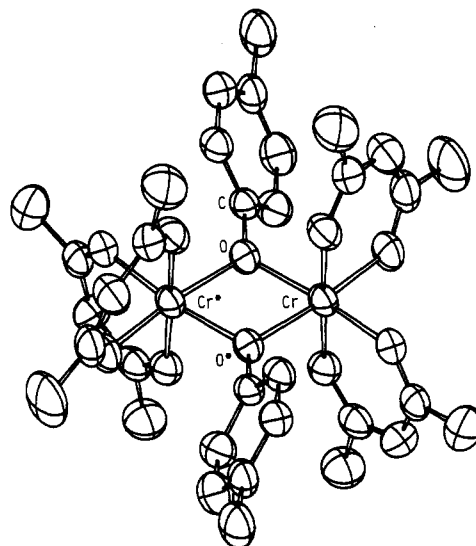


Figure 1. ORTEP drawing of  $[\text{Cr}_2(\text{acac})_4(\text{CH}_3\text{phO})_2]$  (1) at the 50% probability level. Hydrogen atoms are not shown for clarity.

limited number of binuclear complexes bridged by single phenoxo ligands<sup>6</sup> but not by phenoxo groups attached as part(s) of multidentate ligands. Such  $\mu$ -(4-substituted-phenoxo) binuclear complexes of chromium(III) are expected to be one of the most appropriate series which will make possible relating the magnetic interactions to the structural and electronic properties of bridging moieties in comparison with those of similar types of binuclear complexes. We report here a new versatile synthetic route to the novel title binuclear (acetylacetonato)chromium(III) complexes bridged not only by X-phO (X =  $\text{CH}_3$  (1), H (2), Cl (3),  $\text{NO}_2$  (4),  $\text{OCH}_3$  (5)) but also by X-phS (X = H,  $\text{CH}_3$ ) and RO (R = H,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ) together with their characterization, magnetic behavior, and the X-ray structures for two of them (1, 2). Among these complexes, only the alkoxo complexes of analogous types have already been reported.<sup>3,5</sup>

Five phenoxo complexes 1-5 of the  $[\text{Cr}_2(\text{acac})_4(\text{X-phO})_2]$  type were prepared in good yield by the following method. A mixture of an equimolar amount of *trans*- $[\text{Cr}(\text{acac})_2(\text{H}_2\text{O})_2]\text{Cl}$ , 4-X-phenol, and trimethylamine in ethanol was allowed to stand with stirring at room temperature overnight. The color of the solution changed from red to green. The removal of ethanol by a vacuum rotary evaporator gave a green oily residue. From this oily substance, a green complex was extracted with chloroform. After the chloroform was evaporated from this solution, the residue was recrystallized from acetone by refrigeration for a few days. The obtained green crystals were collected, washed with acetone and ether, and dried. The corresponding bis( $\mu$ -4-X-thiophenoxo) complexes were prepared by the same method as mentioned above. The bis( $\mu$ -hydroxo) and bis( $\mu$ -alkoxo) complexes were obtained by the analogous reaction of the starting complex only with trimethylamine in *tert*-butyl alcohol and methanol or ethanol, respectively. It is to be noted that this synthetic method is generally applicable to the binuclear complexes with OR and SR type bridging ligands, which have an extraordinarily wide range of  $\text{p}K_a$  values from 7 to 16.

In view of the elemental analyses,<sup>7</sup> the solubility in chloroform, and the antiferromagnetism as inferred from the magnetic susceptibility measurements, these complexes are supposed to have a binuclear structure. The X-ray single-crystal analyses for

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- Satisfactory elemental analyses for C, H, and/or N or Cr were obtained for all the complexes.

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