Contents lists available at ScienceDirect

# Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# Crystal structure, optical, magnetic, and photochemical properties of the complex pentakis(dimethyl sulfoxide)nitrosylchromium(2+) hexafluorophosphate

Johannes W. Dethlefsen, Anders Døssing\*, Anders Kadziola

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

#### ARTICLE INFO

Article history: Received 7 May 2008 Received in revised form 28 July 2008 Accepted 6 August 2008 Available online 3 September 2008

Keywords: Chromium nitrosyl complexes Solvolysis Photolysis EPR spectra X-ray crystal structure

# ABSTRACT

The nitrosyl complex  $[Cr(dmso)_5(NO)](PF_6)_2$  (1) (dmso = dimethyl sulfoxide) has been prepared by the solvolysis of  $[Cr(NCCH_3)_5(NO)](PF_6)_2$  in neat dmso. The optical absorption spectrum of 1 in dmso shows maxima at 734, 567, 450, 413, and 337 nm. Continuous photolysis of 1 with  $\lambda$  = 365–580 nm light in dmso solution results in a release of NO with quantum yield,  $\Phi$ , in the range 0.034–0.108 mol Einstein<sup>-1</sup>. Irradiation of a deoxygenated CH<sub>3</sub>CN solution of  $[Cr(NCCH_3)_5(NO)](PF_6)_2$  in the presence of excess of  $[Fe(S_2CNEt_2)_2]$  results in a transfer of NO to the iron centre as shown from the characteristic EPR spectrum of  $[Fe(S_2CNEt_2)_2(NO)]$  with  $A_{iso}(^{14}N) = 12.2 \times 10^{-4}$  cm<sup>-1</sup>. The EPR parameters of 1 were determined:  $g_{iso}$ ,  $g_{\parallel}$  and  $g_{\perp}$  : 1.96725, 1.91881(4) and 1.992763(2);  $A_{iso}(^{53}Cr)$ ,  $A_{\parallel}(^{53}Cr)$  and  $A_{\perp}(^{53}Cr)$ : 22.8 × 10<sup>-4</sup>, 39 × 10<sup>-4</sup> and 15.8 × 10<sup>-4</sup> cm<sup>-1</sup>;  $A_{iso}(^{14}N)$ ,  $A_{\parallel}(^{14}N)$  and  $A_{\perp}(^{14}N)$ : 5.9 × 10<sup>-4</sup>, 2 × 10<sup>-4</sup> and 7.540(4) × 10<sup>-4</sup> cm<sup>-1</sup>. (© 2008 Elsevier B.V. All rights reserved.

# 1. Introduction

Nitrosyl complexes of the transition metal ions have attracted attention in recent years owing their ability to release nitric oxide upon photoexcitation. In this regard nitrosyl complexes of iron have been extensively studied as possible sources for nitric oxide [1]. Regarding nitrosyl complexes of chromium, numerous complexes that includes the Cr(NO)<sup>2+</sup> core have been prepared and characterized. Of "homoleptic" complexes, the anionic species  $[CrX_5(NO)]^{3-}$  have been reported for  $X = CN^-$ , NCS<sup>-</sup> and  $N_3^{-}$  [2– 4], and the cationic species  $[CrL_5(NO)]^{2+}$  are known for L = H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>3</sub>CN [5–8]. Compared to the number of studies of the photochemistry of nitrosyliron complexes there are few studies of the photochemical reactivity of the nitrosylchromium(2+) complexes. Bakac has studied the photochemistry of the agua complex [Cr(OH<sub>2</sub>)<sub>5</sub>(NO)]<sup>2+</sup> and found that irradiation of aqueous solutions of this complex with UV light produces nitric oxide and the solvated chromium(II) ion,  $[Cr(OH_2)_6]^{2+}$  [9]. In a recent work [5] we have in preliminary studies shown that also the [Cr(NCCH<sub>3</sub>)<sub>5</sub>(NO)]<sup>2+</sup> complex in acetonitrile solution undergoes a photosensitized NO release with a quantum yield of  $\Phi = 0.55$  mol Einstein<sup>-1</sup> on irradiation with near-UV light. On this background and given the fact that acetonitrile complexes are useful synthetic precursors we have used the complex  $[Cr(NCCH_3)_5(NO)](PF_6)_2$  as a starting material to synthesize the novel complex [Cr(dmso)<sub>5</sub>(NO)](PF<sub>6</sub>)<sub>2</sub> (1) (dmso = dimethyl sulfoxide). We report here the synthesis of **1** along with its crystal structure, optical, magnetic, and photochemical properties.

Inorganica Chimica Acta

# 2. Results and discussion

#### 2.1. Synthesis

Acetonitrile (MeCN) complexes are widely used as synthetic precursors owing to the relative lability of the MeCN ligands. We have earlier shown that the aqua complex  $[Cr(OH_2)_5(NO)]^{2+}$  can be prepared by hydrolysis of  $[Cr(NCCH_3)_5(NO)]^{2+}$  [5]. In the present case, the solvolysis of  $[Cr(NCCH_3)_5(NO)](PF_6)_2$  in dmso is complete within 3 h, as judged from the absorption spectra in Fig. 1, and redbrown crystals of 1 can be isolated by vapour diffusion of CHCl<sub>3</sub> into the equilibrated solution. The complex cation in 1 has earlier been prepared in dmso solution by alkylation of the cyanide ligands in  $[Cr(CN)_5(NO)]^{3-}$  with CH<sub>3</sub>I and subsequent solvolysis of the resulting isonitrile complex [10]. The complex was not isolated as a solid, but EPR parameters close to our values (vide infra) were obtained.

# 2.2. Crystal structure

Large single crystals were obtained as described in Section 3. An ORTEP plot of the cation in **1** is shown in Fig. 2 and details for the crystallographic data and selected bond lengths and angles are compiled in Tables 1 and 2. The chromium centre is surrounded by 5 O-bonded dmso ligands and one NO ligand in a slightly distorted octahedral geometry with the N–Cr–O(equatorial) angles



<sup>\*</sup> Corresponding author. Tel.: +45 353 201 14; fax: +45 353 202 12. *E-mail address:* dossing@kiku.dk (A. Døssing).

<sup>0020-1693/\$ -</sup> see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2008.08.001



**Fig. 1.** Optical absorption spectra recorded during the solvolysis of  $[Cr(NCCH_3)_5(NO)](PF_6)_2$  (2.1 mM) in neat dmso. The spectra were recorded 3, 6, 9, 12, 15, 21, 30, 42, 60 and 90 min after the dissolution of  $[Cr(NCCH_3)_5(NO)](PF_6)_2$ .



**Fig. 2.** Molecular structure of the cation in the complex  $[Cr(dmso)_5(NO)]^{2+}$  with the hydrogen atoms omitted for clarity. The thermal ellipsoids enclose 50% probability.

falling in the range  $91.1-97.3^{\circ}$ . The geometry of the  $Cr(NO)^{2+}$  core is similar to other chromium nitrosyl complexes [3,5,7] being almost linear (176.45(13)°). The average Cr-O(equatorial) distance is 2.011(2)Å compared to the Cr–O(axial) distance being 2.0527(9) Å. In Table 3 bond lengths in similar complexes are shown. Firstly, it is seen that the Cr-O distances in dmso and aqua complexes are similar. Secondly, we note that the Cr-O distances in the nitrosyl complexes are slightly longer than in their homoleptic chromium(III) analogues. The O-S distances fall in the range 1.541–1.544 Å and the Cr–O–S angles in the range 119–122° and this points to an sp<sup>2</sup> hybridized oxygen atom that  $\pi$ -interacts with the sulphur atom. The N-Cr-O-S or O-Cr-O-S torsion angles are far from being  $0^{\circ}$ ,  $\pm 90^{\circ}$  or  $180^{\circ}$  (see Table 2), which suggests that there is no Cr–O  $\pi$ -interaction. Finally, it should be mentioned that an analogous ruthenium complex [Ru(dmso)<sub>5</sub>(NO)](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> has been prepared and structurally characterized [13].

# 2.3. Optical absorption spectrum

A characteristic feature of the absorption spectra of [CrL<sub>5</sub>(NO)] type complexes (charge omitted) is an absorption band  $(\tilde{\nu}_2)$  with

| Table 1   |  |
|---|--|
| Details for the crystallographic data collection and refinement for 1 |  |

| Empirical formula                                       | C <sub>10</sub> H <sub>30</sub> CrF <sub>12</sub> NO <sub>6</sub> P <sub>2</sub> S <sub>5</sub> |
|---|---|
| Formula weight  | 762.59  |
| Wavelength (Å)  | 0.71073   |
| Temperature (K)   | 122(2)  |
| Size (mm)   | $0.53 \times 0.20 \times 0.10$  |
| Crystal system  | orthorhombic  |
| Space group   | Pna2 <sub>1</sub>   |
| a (Å)   | 11.3370(15)   |
| b (Å)   | 24.0790(5)  |
| c (Å)   | 11.007(3)   |
| α (°)   | 90.00   |
| β (°)   | 90.00   |
| γ (°)   | 90.00   |
| $V(Å^3)$  | 3004.7(9)   |
| Ζ   | 4   |
| $D_{\text{calc}} (\text{g cm}^{-3})$                    | 1.686   |
| $\mu$ (mm <sup>-1</sup> )                               | 0.935   |
| F(000)  | 1548  |
| $2\theta$ range (°)                                     | 1.99-36.04  |
| Reflections collected                                   | 87789   |
| Reflections $[I > 2\sigma(I)]$                          | 11764   |
| Data/restraints/parameters                              | 14242/1/335   |
| $R_1, wR_2 \left[ I > 2\sigma \left( I \right) \right]$ | 0.0301, 0.0645  |
| Goodness-of-fit on F <sup>2</sup>                       | 0.994   |
|   |   |

| Table 2  |      |           |         |        |                 |  |
|----------|------|-----------|---------|--------|-----------------|--|
| Selected | bond | distances | (Å) and | angles | (°) in <b>1</b> |  |

| Cr1-N22 | 1.6904(11) | Cr1-N22-021     | 176.45(13) |
|---------|------------|-----------------|------------|
| Cr1-032 | 2.0127(11) | N22-Cr1-072     | 177.89(15) |
| Cr1-042 | 2.0150(11) | N22-Cr1-O32-S31 | -134.86(8) |
| Cr1-052 | 2.0063(11) | N22-Cr1-O42-S41 | -131.29(8) |
| Cr1-062 | 2.0082(11) | N22-Cr1-052-S51 | -53.03(8)  |
| Cr1-072 | 2.0527(9)  | N22-Cr1-062-S61 | -34.47(8)  |
| N22-021 | 1.1963(15) | 052-Cr1-072-S71 | -42.24(7)  |
|         |            |                 |            |

#### Table 3

Cr-O distances in selected chromium complexes

| Complex   | Cr-O <sub>eq</sub> | Cr-O <sub>ax</sub> | Reference |
|---|--------------------|--------------------|-----------|
| 1   | 2.011(2)           | 2.0527(9)          | this work |
| $[Cr(OH_2)_5(NO)]SO_4 \cdot H_2O$                       | 2.012(10)          | 2.0177(9)          | [5]       |
| $[Cr(OH_2)_5(NO)]SO_4$                                  | 1.998(5)           | 2.057(2)           | [6]       |
| [Cr(dmso) <sub>6</sub> ](NO <sub>3</sub> ) <sub>3</sub> | 1.97               | /6(3)              | [11]      |
| $[Cr(OH_2)_6](NO_3)_3 \cdot 3H_2O$                      | 1.95               | 8(4)               | [12]      |

an energy  $(\sim 22 \times 10^3 \text{ cm}^{-1})$  independent of the nature of the L ligands. This has been assigned as a  $\{d_{xz}, d_{yz}, \pi^*(NO)\} \rightarrow \{\pi^*(NO), d_{xz}, d_{yz}\}^*$  transition (Fig. 3) and it is located in the  $[Cr(NO)]^{2+}$  core [14]. In the spectrum of **1** (Fig. 1) we observe in accordance with this a transition with this energy. The lowest energy transition  $(\tilde{v}_1)$  in such complexes has been assigned as a  $\{d_{yz,zx}, \pi^*(NO)\} \rightarrow d_{xy}$  transition, and in **1** it is found at  $13.6 \times 10^3 \text{ cm}^{-1}$ . For comparison  $\tilde{v}_1$  in  $[Cr(OH_2)_5(NO)]^{2+}$  appears as a shoulder around  $15.0 \times 10^3 \text{ cm}^{-1}$  and the energy of the  $d_{xy}$  orbital in **1** is therefore lower than in  $[Cr(OH_2)_5(NO)]^{2+}$ . Since the energy of the  $d_{xy}$  orbital increases with stronger  $\pi$ -donor properties of the L ligand it can be concluded that the dmso ligand is a weaker  $\pi$ -donor than the H<sub>2</sub>O ligand. This is in accordance with the crystal structure (vide supra) that showed the absence of Cr–O  $\pi$ -interaction.

#### 2.4. Photolysis

It has earlier been shown that irradiation of an aqueous solution of  $[Cr(OH_2)_5(NO)]^{2+}$  or MeCN solution of  $[Cr(NCCH_3)_5(NO)]^{2+}$  with UV or near-UV light results in a release of NO [9,5]. However, the



Fig. 3. Orbital splitting diagram for  $[\mbox{CrL}_5(\mbox{NO})]$  (proposed by Gray in Ref. [14]) type complexes.

back-reaction is so fast that in the absence of any trapping agents. such as dioxygen, no net photochemistry occurs during a continuous photolysis. In oxygenated solution oxidative trapping of the solvated chromium(II) ion was observed with the eventual formation of chromium(III) as a result. We have examined the photochemical properties of **1** in dmso solution with and without trapping agents and relevant reactions are outlined in Fig. 4. The photochemical behaviour of 1 parallels that of the two above mentioned nitrosyl complexes. In a deoxygenated dmso solution of 1 no net photochemistry was observed. The photolysis product  $[Cr(dmso)_6]^{2+}$  deserves a comment, since there are no literature reports about this complex. Apart from the complexes [Cr(dmso)<sub>2</sub>Cl<sub>2</sub>], [Cr(dmso)<sub>3</sub>Br<sub>2</sub>] and [Cr(dmso)<sub>4</sub>I<sub>2</sub>], prepared by Holah and Fackler [15], there are no reports in the literature of chromium(II)–dmso complexes. In an attempt to prepare  $[Cr(dmso)_6]^{2+}$ we found that addition of dmso to a rigorously deoxygenated MeCN solution of  $[Cr(NCCH_3)_4(BF_4)_2]$  resulted in the slow formation of green crystals. An X-ray crystallographic investigation of those crystals revealed that the complex [Cr(dmso)<sub>6</sub>](BF<sub>4</sub>)<sub>3</sub>, being isomorphous with the known structure of [Cr(dmso)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub>, had formed [11]. The structure is unfortunately disordered and accordingly not suitable for publication. Apparently Cr(II) is oxidized by dmso, but the interesting point here is, however, that since no net photochemistry occurs in deoxygenated dmso solutions of **1**, the oxidation of  $[Cr(dmso)_6]^{2+}$  by dmso must be much slower than the reaction between  $[Cr(dmso)_6]^{2+}$  and NO. In this context it should be mentioned that the second-order rate constant for the reaction between NO and Cr<sup>2+</sup> in aqueous solution has been



**Fig. 5.** Continuous photolysis of an aerated 7.89 mM dmso solution of  $[Cr(dmso)_{5^-}(NO)](PF_6)_2$  in a 1.000 cm cuvette. The spectra were recorded after 0, 25, 50 min, 1.5, 2.5, 3.5, 5, 9.5, 22, 24, 26.5 and 29 h photolysis.

found to be  $\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [9]. In aerated dmso solutions, where  $[O_2] = 0.42 \text{ mM}$  [16], a net photochemistry is observed as shown in Fig. 5 as a result of oxidative trapping of the  $[Cr(dmso)_6]^{2+}$  complex leading to the formation of a superoxochromium(III) species. We have no experimental evidence for the formation of this species, but we suggest it as a short-lived species in analogy with the behaviour in aqueous solution where the formation of  $[Cr^{III}(H_2O)_5(O_2)]^{2+}$  is well documented [17]. The absorption maxima ( $\lambda/nm$ ,  $\varepsilon/M^{-1}$  cm<sup>-1</sup>) in the final spectrum in Fig. 5 are located at (621, 34.1) and (441, 37.0). Comparison with the spectrum of [Cr(dmso)<sub>6</sub>]<sup>3+</sup> having the absorption maxima (634, 33.4) and (444, 34.6) [18] suggests that the final chromium species is  $[Cr(dmso)_5(OH_2)]^{3+}$  or  $[Cr(dmso)_5(OH)]^{2+}$ . The sharp peaks in the spectra taken during the photolysis at 330-400 nm are characteristic of HNO<sub>2</sub> [19]. This is formed by the reaction between NO, O<sub>2</sub> and traces of water in the solution:

$$4NO + O_2 + 2H_2O \rightarrow 4HNO_2 \tag{1}$$

This reaction follows third-order kinetics in aqueous solution in the pH range 1–13 with the rate law [20]:

$$\frac{d[\text{NO}]}{dt} = -8 \times 10^6 \text{ M}^{-2} \text{ s}^{-1} \text{ [NO]}^2[\text{O}_2]$$
(2)

The reaction:

$$Cr^{2+} + O_2 \rightarrow Cr(O_2)^{2+}$$
 (3)

in aqueous solution follows a second-order rate law [21]:

$$\frac{d[Cr^{2+}]}{dt} = -1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} [Cr^{2+}][O_2]$$
(4)



Fig. 4. Scheme illustrating possible reactions during the photolysis of [Cr(dmso)<sub>5</sub>(NO)]<sup>2+</sup> in dmso.

During the photolysis of a  $[Cr(NO)]^{2+}$  complex we have  $[Cr^{2+}] = [NO]$  and this gives

$$\frac{\frac{d|Cv^2}{dt}}{\frac{d|Cr^{2+}|}{dt}} = 0.05 \text{ M}^{-1} \text{ [NO]}$$
(5)

By assuming that the values of the rate constants in dmso solution do not differ dramatically from those in aqueous solution and since  $[NO] \ll 1$  M, we can conclude that the dominating trapping mechanism is the reaction between dioxygen and the  $[Cr(dmso)_6]^{2+}$  complex (Eq. (3)) and not the reaction between dioxygen and NO (Eq. (1)). In Table 4 the observed quantum yields,  $\Phi$ , defined as the amount of decomposed **1** relative to the amount of absorbed photons, are listed. Based on the orbital splitting diagram in Fig. 3 it would be expected that irradiation in the  $\tilde{v}_2$  band would lead to a weakening of the Cr-N(O) bond with a possible release of NO as a result. It is therefore surprising that the photorelease of NO occurs to the same extent at wavelengths as high as 580 nm. Furthermore,  $\Phi$  at 404 nm in the analogous complex of  $[Cr(NCCH_3)_5(NO)]^{2+1}$ in MeCN was found to be as high as  $0.55 \text{ mol Einstein}^{-1}$ , one order of magnitude higher that in 1. We have no explanation for this behaviour.

### 2.5. EPR spectra

EPR spectra of 1 were recorded in dmso solution at room temperature and in a frozen glass at 66 K as shown in Fig. 6. At room temperature the spectrum is typical for an  $S = \frac{1}{2}$  system with superhyperfine coupling to  ${}^{14}N$  (I = 1). This gives the intense three line splitting and additional less intense lines coming from hyperfine coupling to  ${}^{53}$ Cr (9.5% natural abundance, I = 3/2). A simulation of the spectrum gave the values for  $g_{iso}$  and  $A_{iso}$ shown in Table 5 [25]. From the frozen glass spectrum the anisotropic parameters  $g_{\parallel}$ ,  $g_{\perp}$  and  $A_{\perp}({}^{14}N)$  were calculated by a least-squares fit [25]. The parameters  $A_{\perp}({}^{53}Cr)$  and  $A_{\parallel}({}^{53}Cr)$  were calculated from the positions of the low intensity lines around 3420 and 3650 G, and  $A_{\parallel}(^{14}N)$  was calculated from  $A_{\parallel}(^{14}N) =$  $3A_{iso}(^{14}N) - 2A_{\perp}(^{14}N)$ . For comparison the EPR parameters for other [CrL<sub>5</sub>(NO)] type complexes with L being an oxygen donor ligand are listed in Table 5. It is noted that the values of the hyperfine and superhyperfine constants are quite similar. As seen in Fig. 3 the unpaired electron resides in the  $d_{xv}$  orbital, which is not involved in bonding to the NO ligand. Superhyperfine interaction to <sup>14</sup>N occurs through a spin orbit coupling matrix element between the  $d_{xy}$  and the  $\{d_{yz}, d_{zx}\}$  set of orbitals [26]. The fact that the hyperfine constants  $A_{iso}({}^{53}Cr)$ ,  $A_{\parallel}({}^{53}Cr)$ , and  $A_{\perp}$  (<sup>53</sup>Cr) are very similar in the four complexes indicates that the degree of the covalency of the metal-ligand bonds is similar. The values of the g parameters, or rather the shift ( $\Delta g$ ) from the free electron value:  $\Delta g = 2.002319 - g$ , reflect the energies of the excited states [26]. Again we see that the g values are very similar in the four complexes, which is not surprising since the

#### Table 4

Observed quantum yields,  $\Phi$ , for the photodecomposition of **1** in dmso solution at 298 K defined as the amount of decomposed **1** relative to the amount of absorbed photons

| λ (nm) | $\Phi$ (mol Einstein <sup>-1</sup> ) |
|--------|--------------------------------------|
| 365    | 0.108(6)                             |
| 405    | 0.070(1)                             |
| 436    | 0.046(2)                             |
| 546    | 0.034(5)                             |
| 580    | 0.049(1)                             |
|        |                                      |

<sup>SP</sup> 3400 3450 3500 3550 3600 3650 3700 *B/G* 

**Fig. 6.** Experimental (–) and simulated (----) EPR spectra of  $[Cr(dmso)_5(NO)]^{2+}$ . The spectrum at 298 K was taken of a solution of  $[Cr(NCCH_3)_5(NO)](PF_6)_2$  equilibrated in neat dmso for 3.5 h. For the low-temperature spectrum the same volume of butane-2,3-diole was added to the equilibrated solution and the mixture was cooled to 66 K.

positions of the ligands in the spectrochemical series are similar. As mentioned earlier the cation in **1** has been prepared by McCain in solution with EPR parameters close to the values in Table 5.

In recent years the bis(dithiocarbamato)iron(II) complexes  $[Fe(S_2CNR_2)_2]$  have been used as trapping agents for in vivo detection of nitric oxide [27]. With hydrophilic R-groups, the complexes are water soluble, and very low concentrations of NO have been detected in vivo through the formation of the complexes [Fe(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>(NO)] which have a characteristic threeline EPR spectrum. The advantage of using  $[Fe(S_2CNR_2)_2]$  complexes as trapping agents is that they are X-band EPR silent. In an attempt to confirm that one of the products in the photodecomposition of complexes containing a  $Cr(NO)^{2+}$  core is NO, we have on this background photolysed a deoxygenated MeCN solution of [Cr(NCCH<sub>3</sub>)<sub>5</sub>(NO)](PF<sub>6</sub>)<sub>2</sub> in the presence of excess of  $[Fe(S_2CNEt_2)_2]$ . We chose MeCN as a solvent since the other photolysis product  $[Cr(NCCH_3)_6]^{2+}$  is X-band EPR silent (S = 2) and since this product does not react further, in contrast to  $[Cr(dmso)_6]^{2+}$  as discussed above. In Fig. 7 EPR spectra taken during a photolysis are shown. The EPR spectrum recorded before the photolysis is the spectrum of  $[Cr(NCCH_3)_5(NO)]^{2+}$  which consist of a broad band located at g = 1.98 without structure because of superhyperfine coupling to <sup>14</sup>N in the five MeCN ligands. During the photolysis new bands indeed grow up as the result of the formation of [Fe(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(NO)] as shown in Fig. 7, whereas the broad band from the  $[Cr(NCCH_3)_5(NO)]^{2+}$ complex eventually disappears. From the final spectrum the superhyperfine constant  $A_{iso}(^{14}N)$  in [Fe(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(NO)] can be calculated to  $A_{iso}(^{14}N) = 12.2 \times 10^{-4} \text{ cm}^{-1}$  with  $g_{iso} = 2.0400$ , very close to the published values being  $12.2 \times 10^{-4} \text{ cm}^{-1}$  and 2.0388 [28].

# 3. Experimental

#### 3.1. Reagents and materials

The complexes  $[Cr(NCCH_3)_5(NO)](PF_6)_2$ ,  $[Fe(S_2CNEt_2)_2]$ , and  $[Cr(NCCH_3)_4(BF_4)_2]$  were prepared according to the literature methods [9,29,30]. Solvents were dried with molecular sieves (4 Å) prior to use.

dinio

| Table 5                    |                         |           |              |            |         |       |
|----------------------------|-------------------------|-----------|--------------|------------|---------|-------|
| EPR parameters for various | [CrL <sub>5</sub> (NO)] | complexes | with L being | an oxygen- | donor l | igand |

| Parameter  | [Cr(dmso) <sub>5</sub> (NO)] <sup>2+</sup> | $[Cr(OH_2)_5(NO)]^{2+}$ | trans-[Cr(acac) <sub>2</sub> (OH <sub>2</sub> )(NO)] <sup>a</sup> | trans-[Cr(ehba) <sub>2</sub> (OH <sub>2</sub> )(NO)] <sup>b</sup> |
|--|--|-------------------------|---|---|
| giso   | 1.96725                                    | 1.9674                  | 1.974   | 1.966   |
| $A_{\rm iso}(^{53}{\rm Cr}) (10^{-4} {\rm cm}^{-1})$         | 22.8                                       | 23.4                    | 24.11   | 26.2  |
| $A_{\rm iso}(^{14}\rm N) (10^{-4}  \rm cm^{-1})$             | 5.9  | 5.7                     | 6.76  | 6.0   |
| $g_{\parallel}$  | 1.91881(4)                                 | 1.91741(2)              | 1.940   | 1.913   |
| $s_{\perp}$  | 1.992763(2)                                | 1.994095(3)             | 1.994   | 1.996   |
| $A_{\parallel}(^{53}\mathrm{Cr}) (10^{-4} \mathrm{cm}^{-1})$ | 39   | 38                      | 39.01   | 39  |
| $A_{\perp}(^{53}\mathrm{Cr}) (10^{-4} \mathrm{cm}^{-1})$     | 15.8                                       | 16                      | 16.66   | 16  |
| $A_{\parallel}(^{14}\text{N}) (10^{-4} \text{ cm}^{-1})$     | 2  | 2.37                    | 3.44  |   |
| $A_{\perp}(^{14}\text{N}) (10^{-4} \text{ cm}^{-1})$         | 7.540(4)                                   | 7.364(4)                | 8.42  | 7.5   |
| Reference  | this work                                  | [22]                    | [23]  | [24]  |

<sup>a</sup> acac = acetylacetonate.

<sup>b</sup> ehba = 2-ethyl-2-hydroxobutyrate.



**Fig. 7.** EPR spectra of a 1.4 mM  $[Cr(NCCH_3)_5(NO)](PF_6)_2/12 \text{ mM} [Fe(S_2CNEt_2)_2]$  deoxygenated MeCN solution. The top spectrum was taken of a solution not exposed to light whereas to the spectra below were taken during a photolysis of the solution.

#### 3.2. Preparation of $[Cr(dmso)_5(NO)](PF_6)_2$ (1)

[Cr(NCCH<sub>3</sub>)<sub>5</sub>(NO)](PF<sub>6</sub>)<sub>2</sub> (0.51 g, 0.88 mmol) was dissolved in dmso (5 ml) in a beaker (50 ml). By vapour diffusion of CHCl<sub>3</sub> (20 ml) into the dmso solution in a desiccator under a nitrogen atmosphere, X-ray quality crystals of **1** separated out within one day. The red-brown crystals were washed with CHCl<sub>3</sub> and diethyl ether and dried in vacuo. Yield 0.60 g (90%). Calc. for C<sub>10</sub>H<sub>30</sub>CrF<sub>12</sub>NO<sub>6</sub>P<sub>2</sub>S<sub>5</sub> (762.59): C, 15.75; H, 3.97; Cr, 6.82; N, 1.84; S, 21.02. Found: C, 15.91; H, 3.88; Cr, 6.68; N, 1.79; S, 22.20%. IR (KBr): 1701 cm<sup>-1</sup>, (dmso) 1693 cm<sup>-1</sup> ( $\nu_{NO}$ ). UV–Vis in dmso ( $\lambda_{max}$ /nm,  $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): (734, 7.0), (567, 49), (450, 130), (413, 131), (337, 143).

### 3.3. X-ray crystallography

Intensity data were collected on a single crystal of **1** at 122 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream and graphite monochromatized Mo K $\alpha$  radiation. Data were reduced with EvalCCD [31], the structures solved by direct methods and refined by least-squares against  $F^2$  with shellx97 [32,33] as incorporated in the MAXUS program [34]. Compound **1** crystallizes in the orthorhombic space group *Pna2*<sub>1</sub> (no. 33) [35]. This space group is acentric but the structure is refined as an inversion twin. Data were corrected for absorption. X-ray parameters and statistics are summarized in Table 1.

#### 3.4. Other physical measurements

Elemental analyses of C, H, Cr, N, and S were done at the Microanalytical Laboratory at our Department of Chemistry. Absorption spectra were recorded on a Cary 5E UV-Vis-NIR spectrophotometer. EPR spectra were recorded on a Bruker Elexsys E 500 instrument, operated at X-band, equipped with a frequency counter and a Gauss-meter. The EPR spectra were simulated or fitted by use of a program written by Dr. H. Weihe, University of Copenhagen, 2007. IR spectra were recorded on a FT-IR 1760X instrument. Actinometry was carried out on stirred solutions (V = 3.00 ml) in a thermostatted (T = 298 K), square 1.000 cm quartz cuvette on an optical train by use of an collimated light from a 200 W Hg lamp and  $K_3[Fe(C_2O_4)_3]$  ( $\lambda < 450 \text{ nm}$ ) [36] and  $K[Cr(NCS)_4(NH_3)_2]$  $(\lambda > 450 \text{ nm})$  [37] solutions. The intensity of absorbed light was in the range  $(0.3-2.4) \times 10^{-6}$  Einstein s<sup>-1</sup> l<sup>-1</sup> with concentrations of **1** being ~8 mM. Photolysis of a deoxygenated CH<sub>3</sub>CN solution of  $[Cr(NCCH_3)_5(NO)](PF_6)_2$  and  $[Fe(S_2CNEt_2)_2]$  was carried out using an EPR capillary tube put inside a larger EPR tube sealed with a rubber septa under a nitrogen atmosphere in a glove box. At regular intervals during the photolysis an EPR spectrum of the reaction mixture was taken.

#### Acknowledgement

Mr. Flemming Hansen is thanked for assistance in the crystallographic work.

## **Appendix A. Supplementary material**

CCDC 679054 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica. 2008.08.001.

# References

- [1] (a) P.C. Ford, I.M. Lorkovic, Chem. Rev. 102 (2002) 993;
- (b) P.C. Ford, S. Wecksler, Coord. Chem. Rev. 249 (2005) 1382.
- [2] J.H. Enemark, M.S. Quinby, L.L. Reed, M.J. Steuck, K.K. Walthers, Inorg. Chem. 9 (1970) 2397.
- [3] A. Levina, P. Turner, P. Lay, Inorg. Chem. 42 (2003) 5392.
- [4] R.C. Maurya, D. Sutradhar, S. Rajput, Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 1289.
- [5] A. Døssing, A.M. Frey, Inorg. Chim. Acta 359 (2006) 1681.
- [6] M. Ardon, S. Cohen, Inorg. Chem. 32 (1993) 3241.
- [7] T. Shibahara, H. Akashi, M. Asano, K. Wakamatsu, K. Nishimoto, M. Mori, Inorg. Chem. Commun. 4 (2001) 413.
- [8] S. Clamp, N.G. Connelly, G.E. Taylor, T.S. Louttit, J. Chem. Soc., Dalton Trans. (1980) 2162.
- [9] A. Nemes, O. Pestovsky, A. Bakac, J. Am. Chem. Soc. 124 (2002) 421.

- [10] D.C. McCain, Inorg. Chim. Acta 5 (1971) 611.
- [11] L. Öhrström, G. Svensson, Inorg. Chim. Acta 305 (2000) 157.
- [12] D. Lazar, B. Ribar, V. Divjakovic, C. Meszaros, Acta Crystallogr., Sect. C 47 (1991) 1060.
- [13] E. Zangrando, B. Serli, L. Yellowlees, E. Alessio, Dalton Trans. (2003) 4391.
- [14] P.T. Manoharan, H.B. Gray, Inorg. Chem. 5 (1966) 823.
- [15] D.G. Holah, J.P. Fackler, Inorg. Chem. 4 (1965) 1721.
- [16] J.M. Achord, C.L. Hussey, Anal. Chem. 52 (1980) 601.
- [17] M.E. Brynildson, A. Bakac, J.H. Espenson, J. Am. Chem. Soc. 109 (1987) 4579.
- [18] D.W. Meek, R.S. Drago, T.S. Piper, Inorg. Chem. 1 (1962) 285.
- [19] M.G. Gomes, S.S.S. Borges, L.G.F. Lopes, D.W. Franco, Anal. Chim. Acta 282 (1993) 81.
- [20] (a) D.A. Wink, J.F. Darbyshire, R.W. Nims, J.E. Saavedra, P.C. Ford, Chem. Res. Toxicol. 6 (1993) 23;
  - (b) P.C. Ford, D.A. Wink, D.M. Stanbury, FEBS Lett. 326 (1993) 1;
  - (c) H.H. Awad, D.M. Stanbury, Int. J. Chem. Kinet. 25 (1993) 375.
- [21] (a) Y.A. Alan, G. Czapski, M. Ardon, Isr. J. Chem. 13 (1975) 15;
- (b) R.M. Sellers, M.G. Simic, J. Am. Chem. Soc. 98 (1976) 6145.
- [22] J.W. Dethlefsen, A. Døssing, Inorg. Chim. Acta 362 (2009) 259.
- [23] A. Keller, B. Jezowska-Trzebiatowska, Polyhedron 4 (1985) 1847.
- [24] L.M. Carruthers, C.L. Closken, K.L. Link, S.N. Mahapatro, M. Bikram, J.-L. Du, S.S. Eaton, G.R. Eaton, Inorg. Chem. 38 (1999) 3529.

- [25] H. Weihe, Program for Simulation of EPR Spectra, University of Copenhagen, 2007.
- [26] N. Azuma, Y. Imori, H. Yoshida, K. Tajima, Y. Li, J. Yamauchi, Inorg. Chim. Acta 266 (1997) 29.
- [27] (a) J. Weaver, S. Porasuphatana, P. Tsai, T. Budzichowski, G.M. Rosen, Free Rad. Res. 39 (2005) 1027;
- (b) A.F. Vanin, Methods Enzymol. 301 (1999) 269.
- [28] C.M. Guzy, J.B. Raynor, M.C.R. Symons, J. Chem. Soc. A 19 (1969) 2987.
- [29] R.H. Holm, L.H. Pinolet, R.A. Lewis, J. Am. Chem. Soc. 93 (1971) 360.
- [30] R.T. Henriques, E. Herdtweck, F.E. Kühn, J. Chem. Soc., Dalton Trans. (1998) 1293.
   [31] A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs, J. Appl. Crystallogr. 36 (2003) 220.
- [32] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
- [33] G.M. Sheldrick, SHELXL-97, University of Göttingen, 1997.
- [34] S. Mackey, C.J. Gilmore, C. Edwards, N. Stewart, K. Shankland, MAXUS: Computer Program for the Solution and Refinement of Crystal Structures, Bruker Nonius, The Netherlands, Macscience, Japan & The University of Glasgow, 1999.
- [35] T. Hahn (Ed.), International Tables for Crystallography, Kluwer Academic Publishers, Dordrecht/Boston/London, 2002.
- [36] J.G. Calvert, J.N. Pitts Jr., Photochemistry, Wiley, New York, 1996.
- [37] E.E. Wegner, A.A. Adamson, J. Am. Chem. Soc. 88 (1966) 394.