# Bond distances are not always what they appear to be: discovery and un-discovery of the longest $Cr(v) \equiv N$ triple bond<sup>†</sup><sup>‡</sup>

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The coordination chemistry of  $CrCl_3$  with three pentadentate ligands having the

[1,4,7]-triazacyclononane-1,4-diacetato motif have been investigated. The new resulting six-coordinate Cr(III)-chloro species react cleanly with sodium azide to form the corresponding azido species, which undergo photolysis under irradiation at 419 nm in acetonitrile–water solution to form Cr(V)-nitrido species that are partially hydrolyzed to their corresponding Cr(III)-hydroxo counterparts. Five of these Cr complexes have been characterized by X-ray crystallography. The hydroxo and nitrido species co-crystallize complicating crystal structural refinement. What at first appeared to be the longest Cr=N triple bond distance yet observed (1.66 Å) was found after re-refinement to be an artifact of positional disorder of the Cr atoms of 73% nitrido and 27% hydroxo species. The re-refined Cr=N bond distance is estimated as 1.58 Å, which agrees well with the observed Cr=N stretching frequency of 971 cm<sup>-1</sup> found by IR spectroscopy. UV-vis data for the "nitrido" complexes suggest that they are all three partially hydrolyzed. These results emphasize the care that must be taken in the characterization of compounds that may co-crystallize with structurally similar analogs.

# Introduction

High-valent chromium species have long been of general interest as powerful oxidants for organic synthesis.<sup>1</sup> For example, Cr(v)oxo species are well known to promote epoxidation of olefins, and chromic acid (Cr(VI)) is often used to attack activated hydrocarbon C-H bonds.2 Corresponding high-valent chromiumnitride chemistry is less well developed. The field began in 1981 with the postulation of a Cr(v)-nitrido complex resulting from photolysis of [Cr<sup>III</sup>(salen)(N<sub>3</sub>)]·2H<sub>2</sub>O.<sup>3</sup> In 1983, the crystal structure of  $[Cr^{v}(N)(tpp)](tpp = tetra-tolylporphinate(2-))$  was reported by Groves et al.,<sup>4</sup> providing the first definitive proof for the formation of a Cr≡N moiety. Subsequently, other ligands such as 1,2-bis(2-pyridylcarboxy)-amido)benzene<sup>5</sup> and phthalocyaninate<sup>6</sup> were employed. Recently, a very efficient synthetic "tool" for the preparation of Cr(v)-nitrido complexes was developed by Bendix using atom and/or group transfer reactions,<sup>7,8</sup> which have allowed the synthesis of Cr=N species with mono-, or bidentate ligands, instead of the polydentate ligands necessary in earlier syntheses. Notably, the above compounds have the following common features (1) they are five-coordinate, having squarepyramidal geometry; (2) the Cr $\equiv$ N distance is around 1.56 Å and the Cr<sup>v</sup> ion lies ~0.5 Å above the plane defined by the four equatorial atoms of the ligand; (3) the  $\nu$ (Cr $\equiv$ N) stretching frequency is observed at ~1015 cm<sup>-1</sup>.

In 1996, the first distorted octahedral Cr(v)-nitrido complexes were reported,<sup>9</sup> of the type  $[(tacn)Cr(N)L]^{n+}$  where tacn is 1,4,7triazacyclononane and L is a bidentate ligand such as oxalate, acetonylacetonate, 2-picolinate or *o*-phenanthroline. Later, other six-coordinate Cr(v) complexes derived from the ligand 1,4,8,11tetraazacyclotetradecane (cyclam) were introduced.<sup>10</sup> These complexes differ from the five-coordinate Cr(v)-nitrido complexes in that the Cr $\equiv$ N stretching frequency is observed at lower frequency ~967 cm<sup>-1</sup>. The mean Cr $\equiv$ N bond distance for the six-coordinate species, 1.57 Å, is only slightly longer than in the case of the fivecoordinate species.

We report here some surprising results on Cr(v)-nitrido species supported by pentadentate derivatives of tacn. Such ligands, which are not as well represented as mono or tri-substituted tacn systems, are currently of interest because these macrocycles can be utilized to construct mononuclear octahedral complexes that possess a site for binding and activation of small molecules.<sup>11-14</sup> We have recently reported three new ligands containing the 1,4,7-triazacyclononane-1,4-diacetate motif (Chart 1) and their coordination chemistry with iron,<sup>15</sup> and now report new chromium complexes with these ligands. In this paper, nine octahedral chromium compounds with the ligands shown in Chart 1 have been prepared and characterized. Several of these compounds have been structurally characterized, and we also report a non-trivial crystal structure of a new Cr(v)-nitrido complex, that crystallizes readily with the analogous Cr(III) hydroxo complex, causing an

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unusually long  $Cr \equiv N$  bond distance to appear in the incompletely refined crystal structure, similar to effects first analyzed by Parkin for other metal-ligand multiply bonded systems.<sup>16</sup>

# Discovery of the longest Cr=N triple bond distance

# Preparation of complexes

The Cr(III) complexes of L1, L2, and L3 are conveniently synthesized by reaction of stoichiometric amounts of the ligand and Cr(THF)<sub>3</sub>Cl<sub>3</sub> in refluxing methanol. Reaction of the soformed Cr(III)-chloro species (compounds 1, 2, and 3 having ligands L1, L2, and L3, respectively) with excess NaN<sub>3</sub> furnishes the corresponding Cr(III)-azido species (compounds 4, 5, and 6). Solutions of these deep purple complexes in methanol-water slowly undergo photochemical cleavage (with 419 nm light) of the azido moiety yielding light pink Cr(v)-nitrido complexes (7, 8, and 9). The photolysis process was monitored optically by changes in the color of the species from dark purple to light pink. A solid sample of 9 was prepared; it was established gravimetrically that  $1.0 \pm 0.2$  equiv of N<sub>2</sub>/Cr(III) center evolved from the starting azido-Cr(III) complex. The reactions are summarized in Scheme 1.

$$\begin{array}{rrrr} \text{Li}_2\text{L} + & \text{CrCl}_3(\text{thf})_3 & \longrightarrow & \text{LCrCl} + & 2 & \text{LiCl} \\ & & 1, 2, 3 & & \\ \text{LCrCl} + & \text{NaN}_3 & \longrightarrow & \text{LCrN}_3 + & \text{NaCl} \\ 1, 2, 3 & & 4, 5, 6 & \\ \text{LCrN}_3 & & & \frac{\text{hv}}{\text{LCrN}} + & \text{N}_2 & \\ \text{4}, 5, 6 & & 7, 8, 9 & \\ \end{array}$$

Table 1 Crystal data

#### **Crystal structures**

Crystal structures of one chloro complex, 2, all three azido complexes, 4-6, and one Cr(v)-nitrido complex, 9, were determined by single crystal X-ray crystallography. A summary of structural parameters is given in Table 1 and selected bond lengths are shown in Table 2, except those of compound 9, which will be presented later.

Fig. 1 shows views of **2** and **6**; structures of **4** and **5** are shown in the electronic supplementary information (ESI).<sup>‡</sup> The ligand arrangement in each crystal structure is similar. The coordination spheres of the Cr centers are facially capped by the three N atoms of the tacn backbone with two of the three further coordination sites filled by the O atoms of the appended acetate groups and the sixth site occupied by Cl in the case of **2** or azide for **4–6**. There is a slight trigonal distortion to all of the complexes as evidenced by the deviation of the X–Cr–Y bond angles from 90 ° by ~5 °, where X and Y are *cis* donor atoms to the Cr center. This trigonal distortion coincides with the simplified trigonal geometry of the tacn backbone, and was also observed in the corresponding iron complexes.<sup>15</sup>

The Cr–N bond distances in **2** and **4–6** follow an interesting trend. The Cr–N bond to the alkyl or aryl N atom has a mean distance of 2.1223[8] Å that is significantly longer than the other two Cr–N distances, 2.0614[8] Å and 2.0706[8] Å for the Cr–N distances *cis* and *trans* to the monodentate Cl or N<sub>3</sub> ligand, which are statistically different from each other, though the difference is unlikely to be relevant in a chemically meaningful sense. The

Table 2Selected bond distances (Å) for 2, 4, 5, and 6

2	Cr1–N7 2.0610(9)	Cr1–N4 2.0789(9)	Cr1–N1 2.1238(9)
	Cr1–O16 1.9629(8)	Cr1–O20 1.9840(8)	Cr1–Cl1 2.3082(3)
4	Cr1–O22 1.950(1)	Cr1–O26 1.953(1)	Cr1–N31 2.006(2)
	Cr1–N7 2.052(2)	Cr1–N4 2.073(2)	Cr1–N1 2.112(2)
5	Cr1–N31 2.021(2)	Cr1–N7 2.067(2)	Cr1–N4 2.073(2)
	Cr1–N1 2.125(2)	Cr1–O16 1.964(2)	Cr1–O20 1.951(2)
	Cr2–O60 1.963(2)	Cr2–O56 1.964(2)	Cr2–N71 1.984(2)
	Cr2–N47 2.058(2)	Cr2–N44 2.073(2)	Cr2–N41 2.132(2)
6	Cr1–O22 1.970(2)	Cr1–O26 1.952(2)	Cr1–N31 2.018(2)
	Cr1–N7 2.061(2)	Cr1–N4 2.063(2)	Cr1–N1 2.119(2)

	2	4	5	6	9
Chemical formula	$C_{13}H_{27}ClCrN_3O_6$	$C_{17}H_{23}CrN_6O_4$	$C_{13}H_{24}CrN_6O_{4.5}$	$C_{18}H_{25}CrN_6O_5$	$C_{18}H_{31.3}CrN_{3.7}O_{8.3}$
FW	408.83	427.41	388.38	457.44	484.29
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_{1}2_{1}2_{1}$	$P2_1/n$	Pbca	C2/c
a/Å	6.8717(3)	7.4667(6)	7.2406(2)	13.2255(6)	33.841(1)
b/Å	31.2767(12)	12.8766(9)	27.785(2)	9.4894(4)	6.7077(2)
c/Å	8.6425(4)	18.77939(9)	16.5271(6)	30.5577(12)	18.7774(4)
β/°	108.478(4)	90	96.459(5)	90	97.07(3)
$V/Å^3$	1761.72(13)	1805.5(2)	3303.8(3)	3835.1(3)	4230.0(2)
Ζ	4	4	8	8	8
$\rho_{\rm calcd}/{\rm g}~{\rm cm}^{-1}$	1.541	1.572	1.562	1.585	1.521
Refl. collected/ $2\theta_{max}$	54167/31.06	38954/33	42349/30	38769/30	38270/31.07
No. of params/restr.	231/6	253/0	452/1	272/0	290/18
R. $wR^2(I > 2\sigma(I))$	0.0257.0.0585	0.0475, 0.0796	0.0521.0.0962	0.0577, 0.0986	0.0730, 0.1215
R indices (all data)	0.0342, 0.0619	0.0635, 0.0847	0.0843, 0.1077	0.0848, 0.1071	0.1044, 0.1314



Fig. 1 Thermal ellipsoid plots of (A) 2 and (B) 6 drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

reason for the  $\sim 0.05$  Å elongation of the alkyl or aryl Cr–N bond distance is not readily apparent, but may be explained by a necessary shortening of the other two Cr–N bond distances to allow chelation of the *N*-acetate groups. Other bond distances to chromium fall within expected ranges.

Our initial refinement of the structure of the nitrido complex 9 showed the expected connectivity of the atoms, having the ligand L3 in the same coordination mode as seen in all of the other structures. The most prominent differences between this structure and the other reported structures are the presence of a short Cr-N bond distance of  $\sim 1.66$  Å, tentatively assigned as a Cr $\equiv$ N nitrido unit. In agreement with this formulation is the fact that the Cr atom lies significantly above the mean equatorial  $N_2O_2$ plane by 0.28 Å and that the Cr-N distance trans to the putative nitrido ligand, 2.24 Å, is significantly long as compared to the comparable distances in 2 and 4-6. As discussed above, the average  $Cr \equiv N$  bond lengths in five-coordinate Cr(v)-nitrido species are  $\sim$ 1.56 Å, and those of six-coordinate species are  $\sim$ 1.57 Å. The apparent  $Cr \equiv N$  bond distance in 9, 1.66 Å, is therefore quite puzzling. If this distance were correct, it would be the longest  $Cr \equiv N$  bond distance known, even longer than that found in the  $[Cr(N)(CN)_5]^{3-}$  ion, 1.594(9) Å, having a cyano group *trans* to the nitrido ligand.<sup>17</sup> Further evidence confirming the Cr=N connectivity and confirming its length is therefore necessary.

# Further characterization

## Magnetic susceptibilities and electronic spectra of complexes

Magnetic susceptibilities of solid samples were measured by using a SQUID magnetometer. For the mononuclear azido-Cr(III) complexes, temperature-independent magnetic moments of 3.84  $\mu_{\rm B}$ , 3.80  $\mu_{\rm B}$  and 3.78  $\mu_{\rm B}$  have been observed at 10–300 K for **4**, **5**, and **6**, respectively, which are in good agreement with the d<sup>3</sup> electron configuration of the Cr(III) ion. A temperatureindependent magnetic moment of 1.85  $\mu_{\rm B}$  at 30–290 K has been found for compound **9** in agreement with a species having one

Complexes	$\lambda/\text{nm} (\epsilon/\text{L} \text{mol}^{-1} \text{cm}^{-1})$
4	540 (190), 400 (152), 317 (sh), 268 (4.1 × 10 <sup>3</sup> )
5	548 (172), 403 (118), 310 (sh), 273 ( $3.0 \times 10^3$ )
6	537 (200), 405 (120), 320 (sh), 268 ( $4.5 \times 10^3$ )
7	565 (55), 420 (41), 330 (sh), 270 (sh)
8	567 (46), 427 (42), 328 (sh), 278 (sh)
9	555 (49), 438 (41), 345 (sh), 275 (sh)

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unpaired electron. This data is in notable agreement with the formulation of  $\mathbf{9}$  as a nitrido complex of the d<sup>1</sup> Cr(v) ion.

Table 3 summarizes the UV-vis spectral data, measured in MeCN–H<sub>2</sub>O (1:1) at ambient temperature. In the case of the azido-Cr(III) complexes in roughly octahedral symmetry, two d–d transitions of low intensity in the visible region at ~540 and 400 nm are assigned as  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}(F)$  and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)$ , from which the ligand field splitting energy 10Dq is calculated to be 18 500 cm<sup>-1</sup>, 18 200 cm<sup>-1</sup>, and 18 600 cm<sup>-1</sup> for **4**, **5**, and **6**. Accordingly, the Racah parameter *B* may be estimated from the strong-field approximation without taking into account of the interaction between  ${}^{4}T_{1g}(F)$  and the unobserved  ${}^{4}T_{1g}(P)$ . This gives the values 540 cm<sup>-1</sup>, 550 cm<sup>-1</sup>, and 510 cm<sup>-1</sup> for **4**, **5**, and **6**, respectively. The value of 10Dq is therefore largest for the complex bearing the most electron-donating R group, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, though the effect of other R groups does not significantly affect the electronic structure.

Compounds 7, 8, and 9 display d–d transitions at  $\sim$ 560 nm,  $\sim$ 430 nm and  $\sim$ 330 nm of low intensity, and assignment of these bands will be discussed later (Fig. 2).



Fig. 2 UV-Vis spectra of 6 during photolysis to produce 9.

## EPR spectroscopy

X-Band EPR spectra of the azido-Cr(III) complexes were measured at 10 K in CH<sub>3</sub>CN–H<sub>2</sub>O (1 : 1) solution. Rhombic signals at  $g_y = 4.8$ ,  $g_x = 2.8$  and  $g_z = 1.9$  were observed with broad linewidths, typical for Cr(III) complexes (d<sup>3</sup> electronic configuration, <sup>4</sup>F ground state in  $O_h$  symmetry) of rather low symmetry.



Fig. 3 X-Band EPR spectra of (A) 8 and (B) 9 in 1:1 CH<sub>3</sub>CN–H<sub>2</sub>O solution at 293 K. Microwave frequency: 9.4334 GHz, power: 5.029  $\mu$ W, modulation amplitude: 1.2 mT.

In contrast, the EPR spectra of frozen solutions of **7**, **8**, and **9** in MeCN-H<sub>2</sub>O (1:1) at 10 K showed a broad unresolved line at  $g_{iso} = 1.98$  without any g or hyperfine splitting, presumably due to significant intermolecular interactions. When EPR spectra of fluid solutions were measured at room temperature (Fig. 3), narrow isotropic signals were detected with the typical quartet of hyperfine satellite lines arising from the 9.5% abundant <sup>53</sup>Cr with I = 3/2. Isotropic g values of 1.979, 1.977, 1.977 and coupling constants,  $A_{iso}$  (<sup>53</sup>Cr), of 2.679, 2.705 and 2.647 mT were obtained from simulations for complexes **7**, **8**, and **9**, respectively. No hyperfine splitting from interaction with <sup>14</sup>N nuclei (I = 1) was resolved for any samples, possibly due to motional averaging of anisotropic couplings to the coordinated ligands.<sup>18</sup> Thus the EPR spectra of **7**, **8**, and **9** resemble those of previously published Cr(v)-nitrido species.<sup>18</sup>

## Infrared spectroscopy

The formation of a  $Cr(v)\equiv N$  group should be detectable by infrared (IR) spectroscopy, and, indeed, photolyzed samples of 7, 8, and 9 show a new band in their IR spectra at ~971 cm<sup>-1</sup> that may be assigned to a Cr $\equiv$ N stretch. Also, the strong absorption bands at 2060 cm<sup>-1</sup> of the azido complexes due to the N<sub>3</sub> unit decreased dramatically during photolysis and disappeared completely in the end. The assigned Cr $\equiv$ N stretching frequencies are compared

in Table 4 to those of other six-coordinate and five-coordinate Cr(v)-nitrido complexes. While the  $Cr\equiv N$  stretching frequency in **9** of 971 cm<sup>-1</sup> is lower in energy than many of the other known Cr(v)-nitrido species, it is not as low as would be expected based on an apparent  $Cr\equiv N$  bond distance of 1.66 Å. For example, the compound [(Me<sub>3</sub>tacn)CrN(acac)]ClO<sub>4</sub> has a  $Cr\equiv N$  stretching frequency of 967 cm<sup>-1</sup>, and a  $Cr\equiv N$  bond distance of 1.58 Å.<sup>9</sup>

## Un-discovery of the longest $Cr \equiv N$ triple bond distance

## Computations

We were initially puzzled by the facts that the crystal structure of **9** contained such a long  $Cr \equiv N$  bond distance whereas other physical and spectroscopic data for **9** seemed to indicate that there was nothing unusual about the  $Cr \equiv N$  species. Unable to rationalize such a long  $Cr \equiv N$  distance, we therefore decided to model the structure of **9** using computational methods at the density functional level of theory (DFT). For the computational model, the ligand L3 was truncated to the NH analog as shown in Scheme 2.



Using this truncated model ligand, the corresponding LCrN complex was subjected to a geometry optimization using the BP86 functional, which has been previously used to compute accurate geometries of species having metal-nitrogen triple bonds.<sup>19</sup> The results of the geometry optimization of this model system are shown in Table 5 in comparison to the apparent metal-ligand bond distances in the structure of 9. Notably, the DFT optimized geometry disagrees with the crystallographic result in that a Cr≡N bond distance of 1.55 Å is predicted by DFT instead of the apparently observed 1.66 Å bond distance. Another striking difference in the two structures is that the DFT result predicts a Cr-N bond distance of 2.44 Å for the nitrogen atom trans to the nitrido ligand, whereas the observed distance is 2.24 Å. Because of these computational results, we began to doubt the accuracy of the crystal structure of 9 and initiated a reinvestigation of the crystallographic data.

#### Reinvestigation of the crystal structure of 9

Upon closer inspection of the crystal structure of **9**, we noted that the thermal ellipsoid for the Cr atom was slightly elongated in the direction of the Cr $\equiv$ N bond (Fig. 4). This unusual feature suggests the possibility that the Cr atom may be disordered over two crystallographically independent positions that are close enough to each other that the "average" Cr position appears somewhere in between, and the actual electron density of the Cr centers is covered by the elongation of the thermal ellipsoid of the "average" Cr atom.<sup>20,21</sup> On the other hand, the thermal ellipsoid for the nitrido nitrogen atom is not prolate, nor is the ellipsoid

Complexes	C.N.	Cr≡N/Å	Cr out of plane/Å	$v(Cr\equiv N)/cm^{-1}$	Ref.
Cr(N)(tpp)	5	1.565(6)	0.42	1017	4
Cr(N)(bpb)	5	1.560(2)	0.51	1015	5
Cr(N)(salen)	5	1.544(3)	0.499(3)	1012	3
Cr(N)(bis-8-hgl)	5	1.5549(7)	0.5193(3)	1015	8
Cr(N)(bis-dppd)	5	1.5491(14)	0.4652(6)	1007	8
Cr(N)(bis-pddtc)	5	1.5490(13)	0.7251(13)	991	8
$[Cr(N)Cl_4]^{2-}$	5	1.56(2)		1009	7
$[Cr(N)(NCS)_4]^{2-}$	5	1.545(2)	0.41	1016	18
$[Cr(N)(N_3)_4]^{2-1}$	5	1.541(4)	0.53	1019	18
$[(Me_3tacn)Cr(N)(acac)ClO_4]$	6	1.575(9)	0.30	IR: not detected; Raman: 967	9
trans-[Cr(N)cyclam(MeCN)]	6	1.561(3)	0.265	996	10
trans-[Cr(N)(CN) <sub>4</sub> (py)]	6	1.570(3)	0.261(2)	995	33
$Cr(N)(CN)_5$	6	1.594(9)	1.594(9)	995	17
Cr(N)(NCS) <sub>3</sub> (Phen)	6	1.563(2)	0.28	970	18
7	6			971	This work
8	6			968	This work
9	6	See		971	This work

Table 4 Comparison of known Cr(v)-nitrido species<sup>a</sup>

" 8-hql: 8-hydroxoquinolinate; dppd: 1,3-diphenylpropane-1,3-dionate; pddtc: pyrrolidinedithiocarbamate

Table 5 Structural parameters for 9

	Initial crystal structure	Re-refined crystal structure	DFT
Cr≡N/Å	1.666(2)	1.585(8)	1.553
Cr–N1/Å	2.116(2)	2.118(2)	2.148
Cr–N2/Å	2.061(2)	2.059(2)	2.153
Cr–N3/Å	2.238(2)	2.286(2)	2.437
Cr-01/Å	1.978(2)	1.984(2)	1.941
Cr–O2/Å	1.978(2)	1.999(2)	1.939

for the nitrogen atom *trans* to the nitride. Thus, if the Cr atom is disordered over two positions, there are necessarily *two different* sets of Cr–N bond distances. Such a disorder model was found by Parkin<sup>16</sup> to explain unusual bond lengths in solid solutions, most commonly due to disorder of the ligand positions. Also relevant is recent work on metal–metal multiply bonded species in which the metal atom sites are disordered, initially leading to unusual metal–metal bond distances.<sup>20,21</sup> The most likely explanation for the unusual crystallographic parameters in **9** is that **9** is probably co-crystallized with a second compound that does not have a short Cr $\equiv$ N bond. The most likely possibility for such a compound would be a chromium(III) hydroxo complex, LCrOH, that can be formed by hydrolysis of the Cr $\equiv$ N species.

Further evidence for a disordered Cr atom in **9** is seen from a plot of its electron density. When the Cr atom is refined using anisotropic displacement parameters, its electron density in the N31–N4–N7–O26–Cr mean plane (Fig. S3<sup>‡</sup>) shows significant elliptical distortion. Moreover, isotropic refinement of the Cr atom leads to the appearance of two "lobes" of electron density on either side of the Cr atom that are visible in the difference map (Fig. S4<sup>‡</sup>).

A disorder model assuming co-crystallization of **9** with LCrOH was tested by creating two new Cr positions, about 0.3 Å from each other along the  $Cr \equiv N$  axis, whose occupancies were constrained to sum to 1, and splitting the nitrido N atom into an N atom and an O atom whose occupancies were constrained to be equal to the Cr atom having the short  $Cr \equiv N$  distance and the Cr atom having the longer Cr–O distance, respectively. The metal atoms were refined with isotropic displacement parameters and the N and O atoms



**Fig. 4** Crystal structure of **9** (A) before and (B) after re-refinement of the disordered Cr atom. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms as well as the  $p-C_6H_4OCH_3$  group have been removed for clarity.

were constrained to have the same coordinates and displacement parameters. When free refinement of this structural model failed (the two Cr atoms coalesced into one again), a constraint was used fixing the Cr $\equiv$ N bond distance at 1.55 Å (suggested from the computational result). Addition of this constraint allowed the refinement to converge, and once convergence was achieved, the 1.55 Å constraint was removed and the Cr $\equiv$ N bond distance was refined and converged to a value of 1.585(8) Å with a relative occupancy of 73%. This Cr $\equiv$ N bond distance of 1.585 Å makes sense in the context of the Cr $\equiv$ N bond distance of 1.575 Å found in [(Me<sub>3</sub>tacn)CrN(acac)]<sup>+</sup>,<sup>9</sup> the only structurally characterized Cr(v)nitrido species bearing the tacn moiety as found in **9**.

Thus, the re-refined model of 9 contains  $\sim 27\%$  of an impurity that we propose to be a Cr(III) hydroxo complex, a reasonable assignment considering the possibility of partial hydrolysis of the Cr≡N group. The so-refined Cr–OH bond distance, 1.87(2) Å, is also reasonable considering Cr-OH bond distances known from other Cr(III) complexes (mean of 1.92 Å).<sup>22</sup> The presence of a Cr(III)-hydroxo species in  $\sim 27\%$  of the sample was largely overlooked in the analysis of the spectroscopic features of 9, mainly because we identified features showing the existence of the Cr(v)-nitrido species instead of features associated with its purity. Purity was assumed (incorrectly) because of the crystallinity of the sample. In this connection, it should be mentioned that the elemental analysis data for 9 (Found: C 44.57%, H 6.32%, N 11.40%) are a good fit for [L3CrN]·3H<sub>2</sub>O (Calcd: C 44.72%, H 6.46%, N 11.59%) but may equally well support the formula [L3CrN<sub>0.73</sub>(OH)<sub>0.27</sub>]·3H<sub>2</sub>O suggested by the crystallographic analysis (Calcd: C 44.60%, H 6.45%, N 10.90%). In fact, the electronic spectra of the "nitrido" complexes, which show d-d transitions at  $\sim$ 560 nm,  $\sim$ 430 nm and  $\sim$ 330 nm, more closely resemble spectra of the corresponding Cr(III) species than genuine Cr(v)-nitrido species that typically have the Ballhausen–Gray  ${}^{2}B_{2} \rightarrow {}^{2}E_{1}$  (for a  $C_{4v}$  ML<sub>4</sub> = E species) transition at ~420 nm as their lowest-energy electronic transition.9,23

The corrected structure of **9** brings up important crystallographic issues that have been identified previously in cases of "bond-stretch isomerism" where incorrect metal–ligand or metal– metal bond distances have been assigned due to unresolved crystallographic disorder in crystalline mixtures of structurally similar compounds.<sup>16,20</sup>

# Conclusions

We have therefore shown that new six-coordinate Cr(III)-chloro species 1–3 react cleanly with sodium azide to form the corresponding azido species 4–6. Further photolysis of 4–6 forms Cr(v)-nitrido species 7–9 that are partially hydrolyzed to their corresponding Cr(III)-hydroxo counterparts. The hydroxo and nitrido species co-crystallize complicating the structural refinement of 9. What at first appeared to be the longest Cr=N triple bond distance yet observed (1.66 Å) was found after re-refinement to be an artifact of positional disorder of the Cr atoms of nitrido and hydroxo species. The re-refined Cr=N bond distance is estimated as 1.58 Å, reasonably within the limits of known six-coordinate Cr(v)-nitrido species. UV-vis data for 7–9 suggest that all three nitrido species are partially hydrolyzed. These results emphasize the care that must be taken in the characterization of compounds that may co-crystallize with structurally similar analogs.

# Experimental

## Note

Although we have not encountered any problems in the present study, it should be kept in mind that metal azides are potentially explosive and should be handled carefully in small amounts and with appropriate precaution.

The solvents diethyl ether, toluene, ethanol, dichloromethane, chloroform and *n*-hexane were commercially available and dried over molecular sieves before use; methanol and MeCN were dried over  $CaH_2$  and distilled under argon before use. Other chemicals were obtained from commercial sources and used without further purification.

# Synthesis of ligands and complexes

1,4,7-Triazacyclononane, (tacn) was synthesized as described in the literature.<sup>24</sup> The lithium salts of the corresponding ligands have been synthesized and characterized as reported in the literature.<sup>15</sup> Li<sub>2</sub>L1·2LiOH·H<sub>2</sub>O = {4-carboxymethyl-7-benzyl-[1,4,7]triazonan-1-yl}-acetic acid lithium salt; Li<sub>2</sub>L2·LiOH·2EtOH = {4-carboxymethyl-7-isopropyl-[1,4,7]triazonan-1-yl}-acetic acid lithium salt; Li<sub>2</sub>L3·2LiOH·2EtOH·2H<sub>2</sub>O = {4-carboxymethyl-7-(methoxyl-benzyl)-[1,4,7]triazonan-1-yl}-acetic acid lithium salt.

**[L1CrCl] (1).** To a purple solution of Cr(THF)<sub>3</sub>Cl<sub>3</sub> (374 mg, 1.0 mmol) in MeOH (20 cm<sup>3</sup>) was added Li<sub>2</sub>L1·2LiOH·H<sub>2</sub>O (413 mg, 1.0 mmol) in MeOH (10 cm<sup>3</sup>) at room temperature. The purple color of the solution changed to green and some green precipitates appeared. Zn granules were added and the solution became clear. It was refluxed for 8 h, during which time the color of the solution changed from green, purple to dark purple in the end. The reaction mixture was filtered and slow evaporation of the filtrate at RT led to the formation of purple precipitates, which were dried under vacuum. Yield: 52% (218 mg). Anal. Calcd for the complex L1CrCl (C<sub>17</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>CrCl, 420. 8 g mol<sup>-1</sup>) C 48.52, H 5.51, N 9.99; Found C 48.75, H 5.88, N 10.22. ESI-MS spectrometry (positive mode): m/z = 421 ([L1CrCl]<sup>+</sup>).

[L2CrCl] (2) and [L3CrCl] (3). These compounds were prepared similarly to 1.

**[L2CrCl]·2H<sub>2</sub>O (2).** Recrystallization of the compound in H<sub>2</sub>O–MeOH (3:7) solution resulted in purple crystals after one week. Yield: 56%. Anal. Calcd for the complex L2CrCl·2H<sub>2</sub>O (C<sub>13</sub>H<sub>27</sub>N<sub>3</sub>O<sub>6</sub>CrCl, 408.8 g mol<sup>-1</sup>) C 38.19, H 6.66, N 10.28; Found C 38.02, H 6.83, N 10.70. ESI-MS spectrometry (positive mode): m/z = 395 ([L2CrCl + Na]<sup>+</sup>). IR (KBr cm<sup>-1</sup>): 3456 (s), 1634 (s), 1492 (m), 1453 (w), 1334 (s), 1303 (s), 1168 (w), 1082 (m), 1034 (w), 1005 (m), 922 (s), 852 (m), 827 (m), 721 (m).

**[L3CrCl] (3).** The compound was dried under vacuum. Yield: 63%. Anal. Calcd for the complex L3CrCl ( $C_{18}H_{25}N_3O_5CrCl$ , 450.8 g mol<sup>-1</sup>) C 47.95, H 5.59, N 9.32; Found C 48.22, H 5.30, N 9.07. (ESI-MS spectrometry (positive mode): m/z = 450([L3CrCl]<sup>+</sup>). IR (KBr cm<sup>-1</sup>): 3455 (m), 1670 (s), 1517 (s), 1491 (m), 1456 (m), 1328 (s), 1295 (s), 1254 (m), 1245 (m), 1204 (w), 1180 (w), 1080 (m), 1031 (m), 958 (m), 922 (m), 830 (s), 729 (s), 642 (m), 565 (m).

**[L1CrN<sub>3</sub>] (4).** To a solution of **1** (200 mg, 0.475 mmol) in MeOH (20 cm<sup>3</sup>) was added NaN<sub>3</sub> (309 mg, 4.75 mmol), and the solution was refluxed for 6 h and stirred at RT overnight. Then the reaction mixture was filtered. Slow evaporation of the filtrate in the dark led to the formation of pink crystals suitable for X-ray measurement. Yield: 46% (93 mg). Anal. Calcd for the complex L1CrN<sub>3</sub> (C<sub>17</sub>H<sub>23</sub>CrN<sub>6</sub>O<sub>4</sub>) C 47.77, H 5.42, N 19.66; Found C 48.13, H 5.70, N 19.18. ESI-MS spectrometry (positive mode): m/z = 428 ([L1CrN<sub>3</sub> + H]<sup>+</sup>). IR (KBr cm<sup>-1</sup>): 3455 (m), 2064 (s), 1669 (s), 1492 (m), 1452 (w), 1319 (m), 1287 (m), 1077 (m), 1054 (m), 966 (w), 913 (m), 858 (w), 816 (w), 770 (m), 714 (m), 657 (w).

 $[L2CrN_3]$  (5) and  $[L3CrN_3]$  (6). These compounds were synthesized similarly to 4.

**[L2CrN<sub>3</sub>]·0.5H<sub>2</sub>O (5).** Crystals were obtained from ether diffusion into a MeOH–MeCN solution after two weeks. Yield: 30%. Anal. Calcd for the complex L2CrN<sub>3</sub>·05H<sub>2</sub>O (C<sub>13</sub>H<sub>24</sub>CrN<sub>6</sub>O<sub>4.5</sub>, 388.38 g mol<sup>-1</sup>) C 40.17, H 6.18, N 21.62; Found C 39.87, H 6.06, N 21.23. ESI-MS spectrometry (positive mode): m/z = 402 ([L2CrN<sub>3</sub> + Na]<sup>+</sup>). IR (KBr cm<sup>-1</sup>): 3404 (s), 2067 (s), 1668 (s), 1493 (w), 1460 (w), 1384 (w), 1337 (s), 1303 (w), 1164 (w), 1082 (m), 1065 (m), 1032 (w), 1002 (w), 918 (m), 853 (m), 823 (m), 787 (w), 721 (w).

**[L3CrN<sub>3</sub>] (6).** Purple crystals of **6** suitable for X-ray crystallography were obtained from slow evaporation of MeOH solution at room temperature after one week. Yield: 53%. Anal. Calcd for the compound L3CrN<sub>3</sub> ( $C_{18}H_{25}N_6O_5Cr$ , 457.4 g mol<sup>-1</sup>): C 47.26, H 5.51, N 18.37; Found C 47.60, H 5.44, N 18.69. ESI-MS spectrometry (positive mode): m/z = 480 ([L3CrN<sub>3</sub> + Na]<sup>+</sup>). IR (KBr cm<sup>-1</sup>): 3441 (m), 2060 (s), 1684 (s), 1665 (s), 1511 (s), 1451 (m), 1329 (s), 1290 (s), 1254 (m), 1181 (m), 1081 (m), 1072 (m), 1056 (m), 1021 (s), 954 (w), 921 (m), 832 (m), 722 (m), 666 (w).

 $[L3CrN] \cdot 3H_2O$  (9). A solid sample of 6 (70 mg, 0.153 mmol) was dissolved in 30  $cm^3$  of MeCN-H2O = (1:1) and the resulting purple solution was photolyzed at ambient temperature with Rayonet Photochemical Reactor (RPR-100) equipped with 419 nm tubes. The photolysis process was followed optically by changes in the color of the species from dark purple to light pink for 10 h at room temperature. An EPR measurement of the resulting solution at 10 K shows a typical Cr(v) signal centered at  $g_{iso} = 1.98$ . At the same time, small amounts of photolyzed solution was taken out and allowed to evaporate under vacuum to yield a light pink solid. IR measurements show that the azide stretch at 2060 cm<sup>-1</sup> disappears completely and a new peak due to  $Cr \equiv N$ stretch appears at 971 cm<sup>-1</sup>. Slow evaporation of the solution at room temperature followed by cooling the concentrated solution at 4 °C resulted in the formation of pink crystals suitable for Xray crystallography. Anal. Calcd for the complex L3CrN·3H<sub>2</sub>O (C<sub>18</sub>H<sub>31</sub>CrN<sub>4</sub>O<sub>8</sub>, 483.5 g mol<sup>-1</sup>) C 44.72, H 6.46, N 11.59; Found C 44.57, H 6.32, N 11.40. ESI-MS spectrometry (positive mode): m/z = 452 ([L3CrN + Na]<sup>+</sup>). Yield: 78% (51 mg). IR (KBr cm<sup>-1</sup>): 3430 (m), 1655 (s), 1512 (s), 1364 (m), 1334 (m), 1300 (m), 1251 (m), 1244 (m), 1179 (w), 1086 (w), 1073 (w), 1034 (m), 971 (m), 922 (m), 830 (m), 726 (m), 635 (w).

L1CrN·3H<sub>2</sub>O (7) and L2CrN·2H<sub>2</sub>O (8). These compounds were synthesized in a similar way by photolysis of the corresponding azido-Cr(III) precursors in MeCN–H<sub>2</sub>O (1:1) at 419 nm until the purple color of the solution was bleached and a light pink solution was obtained after 10 h. Anal. calcd for L1CrN·3H<sub>2</sub>O (C<sub>17</sub>H<sub>29</sub>CrN<sub>4</sub>O<sub>7</sub>, 453.4 g mol<sup>-1</sup>) C 45.03, H 6.45, N 12.36; Found C 45.34, H 6.02, N 12.14. ESI-MS spectrometry (positive mode): m/z = 423 ([L1CrN + Na]<sup>+</sup>); IR (KBr cm<sup>-1</sup>): 3428 (s), 1635 (s), 1496 (m), 1461 (w), 1387 (m), 1337 (m), 1297 (m), 1073 (m), 1036 (w), 1010 (m), 971 (m), 925 (m), 858 (w), 838 (w), 816 (w), 767 (m), 710 (m).  $g_{iso} = 1.98$  (10 K).

Anal. Calcd, for L2CrN·2H<sub>2</sub>O ( $C_{13}H_{27}N_4O_6Cr$ , 387.4 g mol<sup>-1</sup>), C 40.31, H 7.03, N 14.46 ESI-MS spectrometry (positive mode): m/z = 352 ([L1CrN + H]<sup>+</sup>); IR (KBr cm<sup>-1</sup>): 3421 (s), 1653 (s), 1492 (w), 1458 (w), 1384 (m), 1336 (m), 1291 (m), 1125 (w), 1094 (m), 1065 (m), 1030 (w), 1006 (w), 968 (m), 925 (m), 822 (s), 727 (m), 629 (w).  $g_{iso} = 1.98$  (10 K).

#### Physical measurements

Infrared spectra (400–4000 cm<sup>-1</sup>) of solid samples were recorded on a Perkin-Elmer 2000 FT-IR/FT-NIR Spectrometer as KBr disks. ESI-MS spectra were recorded on a Finnigan MAT 95 mass spectrometer. UV/Vis spectra of solutions were measured on a Perkin-Elmer Lambda 19 spectrophotometer in the range 200–1000 nm. Temperature-dependent magnetic susceptibilities of powdered samples were measured by using a SQUID magnetometer (Quantum Design) at 1.0 T (2.0–300 K). Corrections for underlying diamagnetism were made by using tabulated Pascal constant. X-band EPR spectra were recorded on a Bruker ESP 300E spectrometer equipped with a helium flow cryostat (Oxford Instruments ESR 910).

Low-temperature EPR, magnetization measurements were analyzed on the basis of a spin-Hamiltonian description of the electronic ground-state spin multiplet

$$H_{\rm e} = D[S_z^2 - S(S+1)/3 + (E/D)(S_x^2 - S_y^2)] + \mu_{\rm B}B\,gS$$

where S = 3/2 or S = 1/2 is the spin of the corresponding system and D and E/D are the axial and rhombic zero-field parameters for S > 1/2.

### X-Ray crystallography

All the crystals were covered with perfluorinated polyether and mounted on glass fibers. Graphite monochromated Mo Ka radiation ( $\lambda = 0.71073$  Å) was used throughout. Intensity data were collected on a Siemens SMART CCD-detector system equipped with a cryogenic nitrogen cold stream at 100 K. Data collection was performed by a hemisphere run taking frames at  $0.30^{\circ}$  in  $\omega$ . The data were corrected for Lorentz and polarization effects. A semiempirical absorption correction using the program SADABS<sup>25</sup> was performed for the compounds. The Siemens SHELXTL<sup>26,27</sup> software package was used for solution, refinement, and artwork of the structures. All the structures were solved and refined by direct methods and difference Fourier techniques. Neutral atom scattering factors were used. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

#### Computations

Calculations were performed using the ORCA program.<sup>28</sup> Geometry optimization utilized a truncated model ligand (Scheme 2) with all atomic coordinates taken from the crystal structure of **9** before re-refinement of the disordered Cr atom. The BP86 functional<sup>29-31</sup> was used in the geometry optimization, with a triple-ζ basis set.<sup>32</sup>

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