

Crystal Structures of *mer*-Cr(pyridine)₃(N₃)₃ and Polymeric NaCr(pyridine)₄(N₃)₄. A Structure Containing $\mu(1,3)$ Bridging Azido Ligands between Chromium- and Sodium-Centered Polyhedra

Mohamed A. S. Goher^a, Morsy A. M. Abu-Youssef^a, and Franz A. Mautner^{b,*}

^a Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

^b Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, Rechbauerstraße 12, A-8010 Graz, Austria

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The structures of *mer*-Cr(py)₃(N₃)₃ (**1**) and polymeric NaCr(py)₄(N₃)₄ (**2**) were determined by X-ray crystallography. Crystal data; **1**, C₁₅H₁₅N₁₂Cr, triclinic, space group P $\bar{1}$, $a = 895.3(2)$, $b = 999.1(3)$, $c = 1269.9(5)$ pm, $\alpha = 106.76(3)^\circ$, $\beta = 96.69(3)^\circ$, $\gamma = 116.30(2)^\circ$, $V = 943.8(6) \cdot 10^6$ pm³, $Z = 2$ and $R_w = 0.038$ for 1736 observed MoK α diffractometer data; **2**, C₂₀H₂₀N₁₆CrNa, monoclinic, space group C2/c, $a = 1561.2(3)$, $b = 1028.8(2)$, $c = 1573.6(4)$ pm, $\beta = 90.70(2)^\circ$, $V = 2527.3(9) \cdot 10^6$ pm³, $Z = 4$ and $R_w = 0.033$ for 1272 MoK α diffractometer data.

The coordination around the chromium(III) ion in the discrete molecules of **1** is six-coordinate with mean distances Cr–N(py) of 210.2(4) pm and Cr–N(N₃) of 200.8(4) pm. The terminal azido ligands are almost linear and asymmetric, the N–N bonds nearer to the metal (118.8(6) to 120.5(7) pm) being significantly longer than the terminal ones (114.7(7) to 115.5(7) pm). In compound **2**, each chromium or sodium cation is six-coordinated by four azido groups and two pyridine molecules. The azido groups act as $\mu(1,3)$ bridging ligands between chromium and sodium octahedra to form a three-dimensional network structure. The chromium atoms are *trans*-coordinated by the pyridine ligands whereas the sodium cations are *cis*-coordinated.

Introduction

Chromium(III) forms a thermally stable, probably monoazido complex, on the addition of potassium azide to a chromium(III) salt in molten KSCN [1]. Various products of the UV photolysis of solutions of chromium(III) azido complexes [CrL(N₃)₂]²⁻ (where L = d-valine-N,N-diacetate, nitrilotriacetate or EDTA) have been separated by ion exchange chromatography and identified as chromium(V) nitride complexes by their EPR, absorption and CD spectra [2]. The only chromium(III) azido complex that has been studied by means of X-ray crystallography is [Cr₄(OH)₆(en)₆](N₃)₆ [3], where the azide groups act as counterions.

During the course of our investigation of metal pseudohalide complexes containing substituted pyridines [4–6], we isolated two new chromium(III) azido complexes with pyridine, *mer*-Cr(py)₃(N₃)₃ and NaCr(py)₄(N₃)₄, in which chromium(III) is directly linked to the azide

groups. In the present work, the coordination geometry and the mode of crystal packing of these complexes are presented, as determined by X-ray crystallography.

Experimental

Preparation, analysis, spectral and magnetic data are given in [7].

X-ray crystallography

Single crystals of both compounds were measured at 300(1) K on a modified STOE 4-circle diffractometer. The cell dimensions were determined from setting angles of 60 (compound **1**) and 46 (compound **2**) reflections, respectively. Intensity data were collected with graphite monochromatized MoK α radiation ($\lambda = 71.069$ pm) and processed in the usual way (corrections: LP factor, absorption correction [8]). Pertinent crystallographic data and processing information are summarized in Table I.

The structures were solved by heavy atom methods. Anisotropic displacement parameters were applied to the Cr, Na, C and N atoms (blocked-matrix least-squares refinements). The H atoms were geometrically positioned and included with

* Reprint requests to Dr. F. A. Mautner.

Compound	1	2
Chemical formula	C ₁₅ H ₁₅ N ₁₂ Cr	C ₂₀ H ₂₀ N ₁₆ CrNa
Formular mass	415.4	559.5
Crystal system	triclinic	monoclinic
Cell constants	<i>a</i> = 895.3(2) pm <i>b</i> = 999.1(3) pm <i>c</i> = 1269.9(5) pm α = 106.76(3) $^\circ$ β = 96.69(3) $^\circ$ γ = 116.30(2) $^\circ$ <i>V</i> = 934.8(6) · 10 ⁶ pm ³	<i>a</i> = 1561.2(3) pm <i>b</i> = 1028.8(2) pm <i>c</i> = 1573.6(4) pm β = 90.70(2) $^\circ$ <i>V</i> = 2527.3(9) · 10 ⁶ pm ³
Space group	P $\bar{1}$	C 2/ <i>c</i>
<i>Z</i>	2	4
F(000)	426	1148
Calculated density	1.435 Mg/m ³	1.470 Mg/m ³
Temperature	300(1) K	300(1) K
Approx. crystal dimensions	0.45 × 0.35 × 0.10 mm	0.45 × 0.40 × 0.25 mm
Data collection limits	2 θ < 60 $^\circ$; <i>hkl</i> : -12, -14, 0/12, 14, 17 ω -scan, $\Delta\omega$ = 1.4 $^\circ$	2 θ < 56 $^\circ$; <i>hkl</i> : -20, 0, 0/20, 13, 20 ω -scan, $\Delta\omega$ = 1.4 $^\circ$
Scan mode		
<i>F</i> _o > 3 σ (<i>F</i> _o)	1736	1272
Least squares parameters	269	184
Linear absorption coefficient	μ (MoK α) = 0.624 mm ⁻¹	μ (MoK α) = 0.500 mm ⁻¹
<i>R</i>	0.038	0.033
<i>R</i> _w	0.038	0.033
Weighting function	10.9062 σ ⁻² (<i>F</i> _o)	1.1619 σ ⁻² (<i>F</i> _o)
Residual electron density	0.25/-0.24 · 10 ⁻⁶ e/pm ³	0.17/-0.27 · 10 ⁻⁶ e/pm ³

Table I. Crystallographic data.

isotropic displacement parameters in the final refinement cycles. The programs DIFABS [8], SHELX-76 [9], SHELXS-86 [10], and the X-RAY SYSTEM [11] were used for all computations. Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [12]. The final positional parameters are listed in Tables II and III. Selected bond distances and bond angles are given in Tables IV and V. Further details on the structure determinations can be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen 2, referring to the deposition number CSD 55440, the names of the authors and the literature citation.

Discussion

The structure determination of the red Cr(py)₃(N₃)₃ has shown the complex to have the meridional conformation. The coordination around the central chromium is approximately octahedral (Fig. 1, Table IV). This complex is similar to *mer*-Co(py)₃(N₃)₃ [13], but the Cr–N(py) bonds (201.3(4) to 211.5(4) pm) are slightly longer than the Co–N(py) bonds (197.0(2) to 198.6(3) pm). The same is true for the Cr–N(N₃) bonds (199.9(4)

Table II. Atomic coordinates (× 10⁴) and equivalent isotropic displacement factors (pm² × 10⁻¹) for **1**. *U*_{eq} was calculated as one third of the trace of the orthogonalized *U*_{ij} tensor.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
Cr	2087(1)	3178(1)	2427(1)	36(1)
N 11	– 308(4)	1490(4)	1375(3)	46(3)
N 12	– 1603(5)	1492(4)	1544(3)	52(3)
N 13	– 2868(6)	1451(6)	1686(5)	89(5)
N 21	4519(5)	4792(5)	3450(3)	50(3)
N 22	5313(5)	6168(5)	3551(3)	47(3)
N 23	6131(6)	7499(5)	3681(4)	89(4)
N 31	1726(5)	5014(4)	2426(3)	49(3)
N 32	530(5)	4932(4)	1838(3)	53(3)
N 33	– 578(6)	4942(5)	1281(4)	86(5)
N 1	1134(4)	3070(4)	3856(3)	44(3)
C 1	1749(6)	4409(5)	4800(4)	50(4)
C 2	1223(6)	4370(7)	5780(4)	63(5)
C 3	26(7)	2905(7)	5772(5)	69(5)
C 4	– 628(7)	1543(7)	4821(4)	64(5)
C 5	– 33(6)	1657(6)	3890(4)	51(4)
N 2	3039(4)	3111(4)	998(3)	39(3)
C 6	4437(5)	2931(5)	954(4)	49(4)
C 7	5007(6)	2758(6)	1(4)	65(5)
C 8	4133(7)	2763(6)	– 956(4)	69(5)
C 9	2739(6)	2996(6)	– 916(4)	61(4)
C 10	2216(5)	3151(5)	67(3)	46(3)
N 3	2624(4)	1351(4)	2526(3)	40(3)
C 11	3658(6)	1593(5)	3494(4)	50(4)
C 12	4072(7)	432(7)	3574(5)	65(5)
C 13	3432(7)	– 974(7)	2661(5)	68(5)
C 14	2386(6)	– 1211(6)	1681(5)	60(4)
C 15	1996(5)	– 38(5)	1633(4)	46(3)

Table III. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors ($\text{pm}^2 \times 10^{-1}$) for **2**. U_{eq} was calculated as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
Cr	2500	2500	0	31(1)
Na	0	191(2)	2500	38(1)
N11	1614(2)	1143(3)	− 270(2)	42(2)
N12	1481(2)	584(3)	− 917(2)	37(2)
N13	1317(2)	0(3)	− 1529(2)	62(2)
N21	3185(2)	1941(3)	− 1019(2)	44(2)
N22	3777(2)	2527(3)	− 1315(1)	40(1)
N23	4348(2)	3051(3)	− 1619(2)	60(2)
N1	1839(2)	3866(3)	− 753(2)	35(2)
C1	2252(2)	4687(3)	− 1269(2)	40(2)
C2	1835(2)	5617(4)	− 1750(2)	50(2)
C3	959(3)	5746(4)	− 1691(2)	55(2)
C4	524(2)	4911(4)	− 1164(2)	53(2)
C5	978(2)	3987(3)	− 709(2)	45(2)
N2	9316(2)	1512(3)	8393(2)	48(2)
C6	9308(2)	1417(4)	9234(2)	49(2)
C7	8853(3)	2237(3)	9749(3)	56(3)
C8	8370(3)	3204(4)	9389(3)	59(3)
C9	8374(3)	3334(4)	8520(3)	59(3)
C10	8852(2)	2468(4)	8054(2)	54(2)

Table IV. Main bond distances (pm) and angles (deg) of **1**.

Cr–N1	210.4(4)	Cr–N2	208.9(4)
Cr–N3	211.5(4)	Cr–N11	201.4(4)
Cr–N21	201.3(4)	Cr–N31	199.9(4)
N11–N12	120.5(7)	N12–N13	115.2(8)
N21–N22	119.2(7)	N22–N23	114.7(7)
N31–N32	118.8(6)	N32–N33	115.5(7)
N1–Cr–N2	175.3(2)	N1–Cr–N3	87.2(2)
N1–Cr–N11	89.9(2)	N1–Cr–N21	91.3(2)
N1–Cr–N31	91.9(2)	N2–Cr–N3	88.1(1)
N2–Cr–N11	89.3(2)	N2–Cr–N21	89.4(2)
N2–Cr–N31	92.8(2)	N3–Cr–N11	90.4(2)
N3–Cr–N21	87.3(2)	N3–Cr–N31	176.0(1)
N11–Cr–N21	177.3(2)	N11–Cr–N31	93.5(2)
N21–Cr–N31	88.9(2)	N11–N12–N13	178.1(6)
Cr–N11–N12	122.7(3)	N21–N22–N23	177.2(6)
Cr–N21–N22	125.2(4)	N31–N32–N33	176.3(5)
Cr–N31–N32	126.8(3)		

Na–N2B	249.4(3)	Na–N13D	255.3(3)
Na–N23A	250.2(3)	Cr–N11	200.7(3)
Cr–N1	210.1(3)	Cr–N21	202.2(3)
N11–N12	118.5(4)	N12–N13	116.2(4)
N21–N22	120.2(4)	N22–N23	115.2(4)
N2B–Na–N13D	87.5(1)	N2B–Na–N23A	90.9(1)
N2B–Na–N2C	90.8(1)	N2B–Na–N13E	86.3(1)
N2B–Na–N23F	178.2(1)	N13D–Na–N23A	93.1(1)
N13D–Na–N2C	86.3(1)	N13D–Na–N13E	171.2(1)
N13D–Na–N23F	93.3(1)	N23A–Na–N2C	178.2(1)
N23A–Na–N13E	93.3(1)	N23A–Na–N23F	87.4(1)
N11A–Cr–N1	89.2(1)	N11–Cr–N21A	89.8(1)
N11–Cr–N1	90.8(1)	N11–Cr–N11A	180.0(1)
N11–Cr–N21	90.2(1)	N1–Cr–N21	90.3(1)
N1–Cr–N1A	180.0(1)	Na–N13D–N12D	134.8(2)
N1–Cr–N21A	89.8(1)	NaA–N23–N22	153.0(3)
N21–Cr–N21A	180.0(1)	Cr–N21–N22	125.5(2)
Cr–N11–N12	129.2(2)	N11–N12–N13	176.3(3)
N21–N22–N23	177.4(3)		

Table V. Main bond distances (pm) and bond angles (deg) of **2**.

Symmetry code: A) $1/2-x, 1/2-y, -z$; B) $1-x, -y, 1-z$; C) $-1+x, -y, -1/2+z$; D) $-x, -y, -z$; E) $x, -y, 1/2+z$; F) $-1/2+x, 1/2-y, 1/2+z$.

to 208.4(4) pm) and Co–N(N₃) bonds (193.5(4) to 196.0(3) pm). These Cr–N distances are within the range of 194 to 215 pm found for Cr–N distances in other chromium(III) compounds [14]. The Cr–N(py) bonds are also slightly longer than the Cr–N(N₃) distances as found in the structure of Zn(py)₂(N₃)₂ with terminal azido ligands [15]. The three azido ligands in compound **1** are almost li-

near and asymmetric, and in all of them the longer N–N distance is that between the central nitrogen and the nitrogen coordinated to the chromium atom.

The structure of the green compound NaCr(py)₄(N₃)₄ (Fig. 2, 3, Table V) is similar to the structures of M(py)₂(N₃)₂ (M = Cd [16] or Mn [17]) compounds. The cell dimensions and the vol-

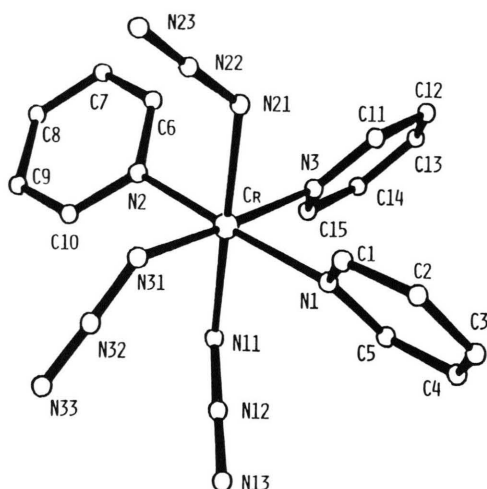


Fig. 1. Perspective view showing molecular structure of the red complex **1**, *mer*-Cr(py)₃(N₃)₃, with atom numbering scheme.

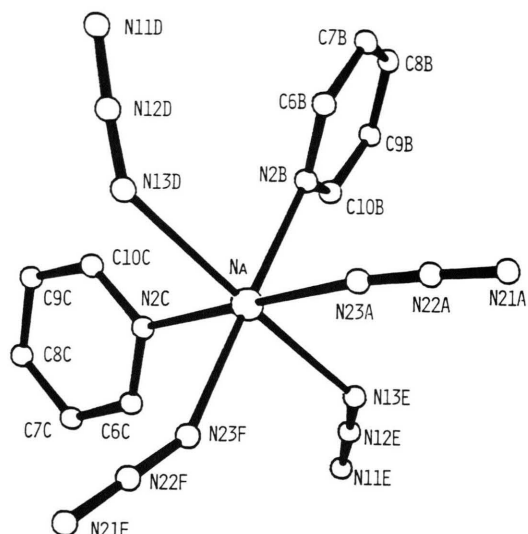


Fig. 3. A perspective view showing the sodium polyhedron in the green complex **2**, NaCr(py)₄(N₃)₄, with atom numbering scheme.

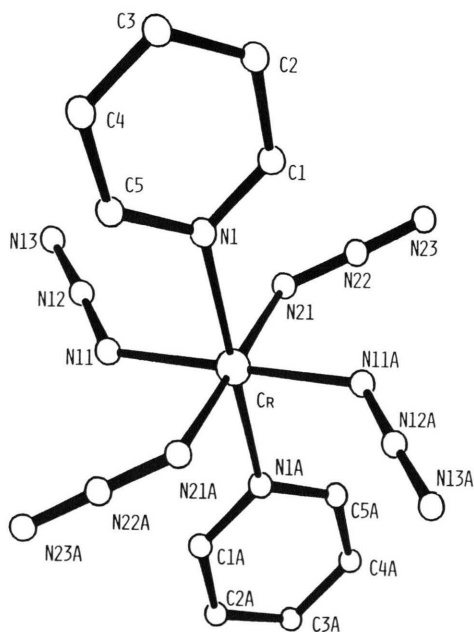


Fig. 2. A perspective view showing the chromium polyhedron in the green complex **2**, NaCr(py)₄(N₃)₄, with atom numbering scheme.

ume of the unit cell are almost identical with that of the cadmium compound. This means that the structure formed by the divalent metals (Cd and Mn) is also favored in the case of the trivalent chromium ion. For reason of charge equivalence sodium atoms substitute every second metal site.

The chromium atom occupies the special position (1/4, 1/4, 0) at inversion centers, the sodium ion the special position (0, *y*, 1/4). As in the cadmium compound, each chromium or sodium cation is six-coordinated to four azido ligands and two pyridine molecules. The azido groups function as $\mu(1,3)$ bridging ligands between chromium and sodium octahedra to form a three-dimensional network. In contrast to the structures of the cadmium(II) and manganese(II) compounds a different kind of network is formed in compound **2**. In the former crystal structures each cadmium (or Mn) center is *trans*-coordinated by the pyridine ligands. In the case of **2**, only the chromium atoms have *trans*-conformation whereas the sodium cations are *cis*-coordinated by the pyridine ligands.

Bond distances and angles within the chromium octahedra (Fig. 2) as well as the geometries of the pyridine ligands are very similar in both compounds (Tables IV and V). Despite the fact that the azido ligands function as monodentates and as $\mu(1,3)$ bridges in compound **1** and **2**, respectively,

their N–N distances are similar in both cases. In fact one of the two azido groups, N11–N12–N13, in complex **2** may be considered as symmetrical, since $\delta\text{N–N}$ is only 2.3 pm [18] ($\delta\text{N–N}$ being the difference between N–N distances in an azide group). However in both $\mu(1,3)$ azido ligands the N–N distances between the central nitrogen and the nitrogen coordinated to the chromium atoms are longer (118.5(4) and 120.2(4) pm) than those

between the central nitrogen and the nitrogen coordinated to the sodium ions (116.2(4) and 115.2(4) pm). The Na–N distances of 250.2(3) and 255.3(3) pm within the sodium octahedra (Fig. 3, Table V) are shorter than those (261–264 pm) in other similar NaN_6 coordination octahedra [19].

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