

Synthesis and Characterization of the Nickel and Cobalt Complexes of New BF_2^+ Bridged, 1,2-Benzoquinone Bis (α -Dioxime) Macrocycles

¹AHMAD S. ABUSHAMLEH* AND ²MUSTAFA M. EL-ABADELAH

¹Chemistry Department, The Hashemite University, Zarqa, P.O.Box. 150459, Jordan

²Chemistry Department, University of Jordan, Amman, 11942, Jordan

(Received 24th February, 2000, revised 2nd August, 2000)

Summary: The synthesis, characterization and structure of new cobalt and nickel complexes with a BF_2^+ bridged, bis (1,2-dione dioxime) ligand based on benzoquinone are described. The crystal structure of the bis (BF_2^+) bridged nickel complex has space group $C2/c$ (#15) with unit cell dimensions $a = 19.000$ (2), $b = 5.452$ (2), $c = 16.357$ (1) Å, $\beta = 119.251$ (7)°, $V = 1519.8$ (2) Å³, $Z = 4$, $R_1 = 0.043$ and $wR_2 = 0.052$. The ligand provides strong field and the complexes are diamagnetic. The spectral properties of the complexes are discussed.

Introduction

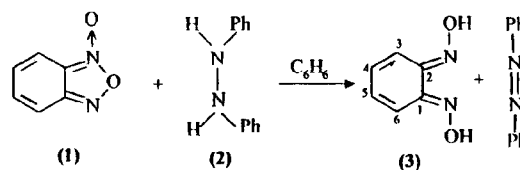
The aromatic compound 1,2-benzoquinone dioxime (bqdH, **3**) had been known for a long time [1] and its synthetic procedures were modified over the years [2,3]. Derivatives of bqdH were reported to be used in the manufacturing of azine dyes [4] and as plant protectants [5] and in neoplasm chemotherapy [6]. The dioxime bqdH has also been used to synthesize 1,2,5-selenadiazole N-oxides, analogues of 1,2,5-oxadiazole N-oxides and 1,2,5-thiadiazole N-oxides [7]. Little attention, however, has been paid to this bidentate ligand with respect to the synthesis of coordination compounds. Previous studies of the metal complexes of bqdH have been largely limited to square-planar derivatives of d^8 metal ions (Ni(II), Pd(II), and Pt(II)) [8], where compounds of columnar stack-type structure were produced [9]. In addition, bqdH produced with platinum (IV), compounds which possess anisotropic optical and conduction properties [10,11]. In recent years, Stynes and coworkers reported on the electronic effects on axial ligation of $\text{Fe}(\text{bqd})_2$, [12,13] and the electrochemical properties of low-spin trans- $\text{Fe}(\text{bqdBF}_2)_2\text{TL}$ [14]. We report here the synthesis, spectral and structural properties of $[\text{Ni}(\text{bqdBF}_2)_2]$ (**5**) and $[\text{Co}(\text{bqdBF}_2)_2(\text{py})\text{F}]$ (**7**).

Results and Discussion

Synthesis and characterization of $[\text{Ni}(\text{bqdBF}_2)_2]$ (**5**)

The multistep synthesis of this compound involves preparation of the 3,5-cyclohexadiene-1,2-dione dioxime ligand (**3**) and consecutive synthesis

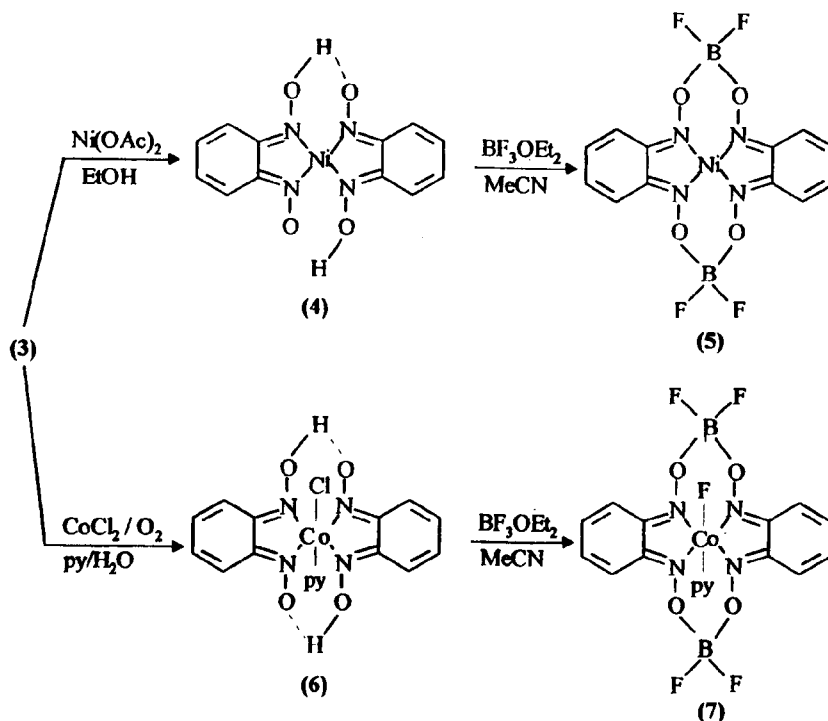
of the nickel(II) complex of that parent dioxime, $[\text{Ni}(\text{bqd})_2]$ (**4**), followed by substitution of bridging protons by BF_2^+ . The method of preparation of the 1,2-dione dioxime, shown in scheme-1, involves the reduction of benzofuroxan (**1**) with hydrazobenzene



Scheme 1

(**2**) in benzene. This method was adapted as described in the literature [3]. The complex $[\text{Ni}(\text{bqd})_2]$ (**4**) was prepared, as illustrated in scheme-2, via the reaction of (**3**) with nickel acetate tetrahydrate in ethanol. The yield was almost quantitative. This complex (**4**) was described by Belombe [9] as being prepared from nickel (II) chloride in a rather lengthy procedures. Elemental analysis, IR, NMR and mass spectral data are in accord with structure (**4**). A reduction in the stretching frequency of C=N in (**3**) was observed upon coordination and is attributed to delocalization of the π -electrons upon complex formation [9]. In addition, the O-H stretching frequency was absent in (**4**) due to the engagement of this group in bridging (O...H...O). The complex is neutral and diamagnetic ($10^6 \chi_M \sim 0$) which is consistent with square planar

*To whom all correspondence should be addressed.



geometry around the nickel atom. This is to be expected considering the planarity of the dioxime ligand and the electronic nature of nickel (II) being a d^8 system. The template synthesis of the new macrocyclic nickel(II) complex $[\text{Ni}(\text{bqdBF}_2)_2]$ (5) was carried out by adding boron trifluoride etherate to an acetonitrile solution containing the proton-linked precursor (4), according to synthetic procedure for analogous systems [15]. The bridging protons were replaced by BF_2^+ groups and a 14-membered tetraazamacrocycle (5) was obtained. This macrocyclic complex is, as expected, electrically non-conducting and diamagnetic ($10^6 \chi_g = -0.044$). The ir spectrum shows $\nu \text{C}=\text{N}$ at 1610 cm^{-1} which is lower than $\nu \text{C}=\text{N}$ in the free ligand due to delocalization of the π -electrons upon complexation. The crystal structure of this complex was determined by X-ray diffraction. The molecular structure is shown in Figure 1, and selected crystallographic data are presented in Tables 1-3. It is apparent from the figure that the macrocycle is planar with the exception of the difluoroborn moieties which are situated such that one is above the plane, while the other falls below the macrocyclic face giving rise to a

chair-like structure. The molecule (5) is highly symmetric and Fig. 2 represents the asymmetric unit from which the rest of the molecule can be generated by the symmetry of the crystal.

Synthesis and characterization of $[\text{Co}(\text{bqdBF}_2)_2(\text{py})(\text{F})]$ (7)

The complex (7) was prepared as illustrated in scheme 2. The synthetic procedure for $[\text{Co}(\text{bqd})_2(\text{py})(\text{Cl})]$ (6), precursor of (7), was adapted from that for the parent compound in this family, $[\text{Co}(\text{MeGlyoxH})_2(\text{py})(\text{Cl})]$ [16]. It was necessary to use the exact stoichiometric amount of pyridine and to perform this reaction in the presence of water. This complex is neutral and almost diamagnetic ($10^6 \chi_g = +0.92$) consistent with $\text{Co}(\text{III})$, d^6 in a strong octahedral ligand field. The $\nu \text{C}=\text{N}$ is also shifted to lower frequency (1595 cm^{-1}) as observed in the nickel complex (4). The template synthesis of the macrocyclic $\text{Co}(\text{III})$ complex $[\text{Co}(\text{bqdBF}_2)_2(\text{py})(\text{F})]$ (7) was performed by adding boron trifluoride etherate to a refluxing acetonitrile solution containing the proton-linked precursor (6).

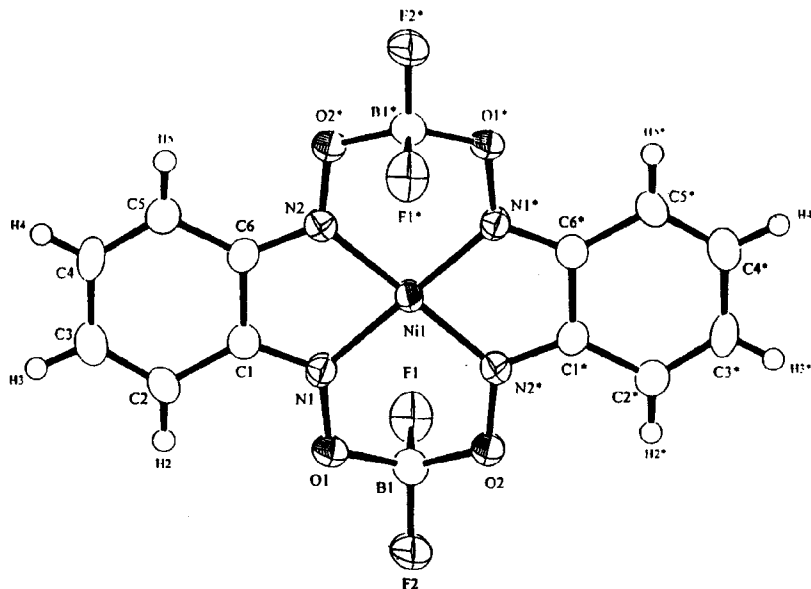


Fig. 1: ORTEP plot of the molecular structure of (5)

Table-1: Fractional atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}
Ni(1)	0.2500	0.2500	0.5000	2.18(1)
F(1)	0.08015(9)	0.4776(3)	0.4904(1)	4.00(4)
F(2)	0.08454(9)	0.8790(3)	0.4522(1)	4.25(4)
O(1)	0.1237(1)	0.5849(3)	0.3840(1)	2.68(4)
O(2)	0.2017(1)	0.6917(3)	0.5543(1)	2.74(4)
N(1)	0.1639(1)	0.3735(4)	0.3915(1)	2.27(4)
N(2)	0.2508(1)	0.0106(4)	0.4198(1)	2.35(4)
C(1)	0.1452(1)	0.2518(5)	0.3150(2)	2.30(5)
C(2)	0.0841(2)	0.3060(5)	0.2208(2)	2.55(6)
C(3)	0.0746(2)	0.1551(5)	0.1516(2)	2.91(6)
C(4)	0.1243(2)	-0.0600(6)	0.1689(2)	3.32(7)
C(5)	0.1823(2)	-0.1225(5)	0.2551(2)	2.61(6)
C(6)	0.1961(1)	0.0341(4)	0.3318(2)	2.23(5)
B(1)	0.1201(2)	0.6556(6)	0.4705(2)	2.74(7)
H(2)	0.055(2)	0.439(5)	0.209(2)	3.1(6)
H(3)	0.035(2)	0.180(5)	0.085(2)	3.9(6)
H(4)	0.114(1)	-0.156(5)	0.122(2)	3.0(6)
H(5)	0.214(2)	-0.257(5)	0.267(2)	2.7(6)

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*) \cos \gamma + 2U_{13}(aa^*cc^*) \cos \beta + 2U_{23}(bb^*cc^*) \cos \alpha)$$

The bridging protons were replaced by BF_2^+ groups and the single mole of axial base, pyridine, was retained. In addition, the chloride present as an axial ligand in (6) was replaced by a fluoride ligand. This is a surprising result because of the substitutional inertness of Co(III); also this is contrary to what was observed in structurally similar systems where the chloride ligand was retained [17,18]. The macrocycle (7) was characterized by mass

Table-2: Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	0.0267(3)	0.0305(4)	0.0212(3)	0.0044(3)	0.0082(3)	-0.0013(3)
F(1)	0.0417(9)	0.063(1)	0.051(1)	-0.0109(8)	0.0260(8)	-0.0052(9)
F(2)	0.056(1)	0.049(1)	0.0454(9)	0.0265(9)	0.0165(8)	0.0026(8)
O(1)	0.0341(9)	0.033(1)	0.0295(9)	0.0108(8)	0.0133(8)	0.0028(8)
O(2)	0.0336(9)	0.033(1)	0.030(1)	0.0081(8)	0.0104(8)	-0.0016(8)
N(1)	0.029(1)	0.031(1)	0.024(1)	0.002(1)	0.0113(9)	-0.004(1)
N(2)	0.029(1)	0.031(1)	0.024(1)	0.003(1)	0.0100(9)	0.0005(9)
C(1)	0.029(1)	0.030(1)	0.027(1)	-0.003(1)	0.013(1)	-0.001(1)
C(2)	0.030(1)	0.036(2)	0.026(1)	0.002(1)	0.009(1)	0.005(1)
C(3)	0.032(1)	0.046(2)	0.026(1)	-0.007(1)	0.010(1)	0.000(1)
C(4)	0.049(2)	0.046(2)	0.027(2)	-0.008(1)	0.016(1)	-0.012(1)
C(5)	0.035(1)	0.035(2)	0.050(1)	0.000(1)	0.016(1)	-0.001(1)
C(6)	0.033(1)	0.028(1)	0.025(1)	-0.005(1)	0.015(1)	-0.003(1)
B(1)	0.030(2)	0.039(2)	0.033(2)	0.009(1)	0.013(1)	0.002(1)

The general temperature factor expression $\exp(-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table-3: Selected Bond Lengths (Å) and Angles (°)

atom	atom	distance	atom	atom	distance
Ni(1)	N(1)	1.856(3)	C(5)	C(6)	1.432(5)
Ni(1)	N(2)	1.855(3)	F(2)	B(1)	1.354(5)
F(1)	B(1)	1.366(5)	O(1)	B(1)	1.300(5)
O(1)	N(1)	1.354(4)	O(2)	B(1)	1.498(5)
O(2)	N(2)	1.356(4)	N(2)	C(6)	1.306(5)
N(1)	C(1)	1.303(5)	C(1)	C(6)	1.470(5)
C(1)	C(2)	1.436(5)	C(2)	H(2)	0.88(4)
C(2)	C(3)	1.337(6)	C(3)	H(3)	0.94(4)
C(3)	C(4)	1.444(6)	C(4)	H(4)	0.87(4)
C(4)	C(5)	1.342(6)	C(5)	H(5)	0.91(4)

atom	atom	atom	angle	atom	atom	atom	angle
Ni(1)	Ni(1)	N(1)	180.0	F(1)	B(1)	O(2)	108.8(3)
Ni(1)	Ni(1)	N(2)	96.5(1)	F(2)	B(1)	O(2)	105.4(4)
Ni(1)	Ni(1)	N(2)	83.5(1)	N(2)	Ni(1)	N(2)	180.0
Ni(1)	O(1)	B(1)	114.6(3)	N(2)	O(2)	B(1)	114.3(3)
Ni(1)	N(1)	O(1)	126.1(2)	Ni(1)	N(1)	C(1)	115.7(3)
O(1)	N(1)	C(1)	118.0(3)	Ni(1)	N(2)	O(2)	125.9(2)
Ni(1)	N(2)	C(6)	113.7(3)	O(2)	N(2)	C(6)	118.2(3)
Ni(1)	C(1)	C(2)	128.6(4)	N(1)	C(1)	C(6)	112.7(3)
N(2)	C(6)	C(1)	112.4(3)	F(1)	B(1)	O(1)	109.2(4)
N(2)	C(6)	C(5)	127.9(4)	F(2)	B(1)	O(1)	105.7(3)
F(1)	B(1)	F(2)	114.6(4)	O(1)	B(1)	O(2)	113.2(3)

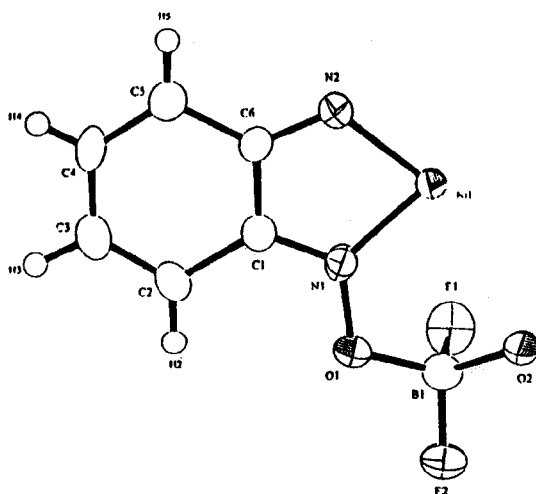


Fig. 2: ORTEP plot of the asymmetric unit of (5)

spectrometry where the usual chloride isotopic pattern is absent from the spectra; the elemental analysis shows no chlorine in compound (7). This compound is neutral and again contains some paramagnetic impurities ($10^6 \chi_g = + 1.03$). These paramagnetic impurities in the cobalt complexes have prevented the determination of reasonable NMR spectra. Compound (7) however, is obtained in poor yield despite many attempts of varying the reaction conditions. It is worth noting that cobaloximes in the trivalent state, such as (7), are remarkably stable toward acid hydrolysis and the complex (5) shows comparable stability. These remarks are in accordance with previous findings [19]. Considerable amount of attention has been given to such complexes as they represent models for vitamin B₁₂ [20]. Related cobalt (III) complexes have been reduced to cobalt (II) and the resulting complexes have demonstrated significant affinity for dioxygen binding [18].

Experimental

Melting points (uncorrected) were determined using a Gallenkamp melting point apparatus in one-end open glass capillaries. IR spectra (KBr pellets) were run on a Fourier Transform Infrared Spectrometer, Magna-IR 560 Nicolet. Mass susceptibility values (χ_g) for solid samples of compounds 4-7 were determined at ambient temperature by the Evans method using a Johnson Matthey Magnetic Susceptibility Balance. UV-Vis

absorption spectra were measured on a Unicam Model Helios alpha double beam scanning UV-Visible Spectrometer 9423 UVA 1000E (PC for vision software). NMR spectra were recorded on a Bruker WM-400 spectrometer for solutions in DMSO-*d*₆ or CD₃CN with TMS as internal reference. MS-FAB spectra were obtained with a VG Analytical Ltd. ZAB HS mass spectrometer equipped with xenon gun operating at 8 keV and 0.8 mA emission using as the sample containing matrix, TG/G, CHCl₃ (thioglycerol/ glycerol) or NBA (3-nitrobenzyl alcohol). Elemental analyses were performed at the laboratories of Quantitative Technologies Inc. (QTI), New Jersey, USA.

Preparation of 3,5-cyclohexadiene-1,2-dione dioxime(bqdH) (3)

This compound was prepared by reducing benzofuroxan (1) with hydrazobenzene (2) in benzene according to the literature procedure [3]. Yield : 65%. Recrystallization from THF/CHCl₃ solvent pair system afford analytically pure sample. m.p. 148-150°C (dec.) Lit. [3] m.p. = 151-152°C). Analysis for C₆H₆N₂O₂ (138.13): Calcd C, 52.17; H, 4.38; N, 20.28%. Found C, 52.39; H, 4.46; N 20.20%. IR (ν): 3500-2500 (O-H), 1630 cm⁻¹ (C=N), UV-Vis spectrum (THF): λ_{max} 396 nm, MS POS FAB (Gly/THF) = 139 corresponding to [M + H]⁺ and consistent with C₆H₆N₂O₂. In addition, another very strong peak was observed at 277 m/e corresponding to [2M + H]⁺. This is believed to be due to the dimerization of 3 via H-bonding in the vapor phase. ¹H-NMR(DMSO-*d*₆): δ 6.44 (2H, H-4/H-5, dd, J = 7.9 Hz/3.1 Hz), 7.06 (2H, H-3/H-6, dd, J = 7.9 Hz/3.1 Hz), 12.18 (2H, 2OH, brs). ¹³C-NMR : δ 117.6 (C-4/C-5), 127.6 (C-3/C-6), 147.7 (C-1/C-2).

Preparation of Bis-(3,5-cyclohexadiene-1,2-dione dioximato)nickel (II) [Ni(bqd)₂] (4)

2.0 g (8 mmol) nickel acetate tetrahydrate dissolved in hot 95% ethanol (100 ml) was filtered onto a hot solution of 2.22 g (16 mmol) 3,5-cyclohexadiene-1,2-dione dioxime (3) in 95% ethanol (60 ml). The deep-black reaction mixture was refluxed with continuous stirring for 1 h. The volume was then reduced to about 50 ml and the black solid product was filtered off, washed with hot ethanol and dried in vacuo. Yield: 2.60 g (98%), m.p. > 300°C. For a sample recrystallized from

chloroform: Analysis for $\text{Ni}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_2 \cdot 0.5 \text{H}_2\text{O}$ (341.95): Calcd. C, 42.15; H, 3.24; N, 16.39%. Found C, 41.91; H, 3.01; N, 16.13%. IR (ν): 1596 cm^{-1} (C=N), UV-Vis spectrum (CHCl_3): λ_{max} 456 nm, MS POS FAB (NBA) = 332 corresponding to $[\text{M} + \text{H}]^+$, MS POS FAB exact mass = 332.0056. These values are consistent with $\text{Ni}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_2$. $^1\text{H-NMR}$ (DMSO-d_6): δ 6.70 (4H, br d), 6.87 (4H, br d), 17.07 (2H, 2OH, br s). $^{13}\text{C-NMR}$: δ 116.4; 130.4; 147.5.

Preparation of [1,1,8,8-tetrafluoro-4,5,11,12-di(1',3'-butadiene)-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-1,8-dibora-cyclotetradeca-3,5,10,12-tetraene]nickel (II), $[\text{Ni}(\text{bqdBF}_2)_2]$ (5)

1.0 g (3 mmol) of $[\text{Ni}(\text{bqd})_2]$, (4) was added to 100 ml of freshly distilled acetonitrile and the resulting suspension was kept under an atmosphere of nitrogen. To this suspension 1.5 ml (12 mmol) boron trifluoride etherate was added slowly with continuous stirring to give a deep-red solution. The reaction mixture was stirred at room temperature for 1.5 h. The solvent was removed under reduced pressure and the residue was extracted with two 50 ml portions of acetonitrile and evaporated to dryness. Finally the residue was dissolved in 50 ml of acetonitrile and heated briefly and filtered. The filtrate was set aside in an open flask overnight in the fume hood. Silver metallic-like crystals were obtained. These were filtered off, washed with cold acetonitrile and dried in vacuo. These crystals were used for the X-ray work. Further quantity of the product was obtained by reducing the volume of the filtrate. Total yield: 0.96 g (75%), m.p. > 300°C. Analysis for $\text{NiC}_{12}\text{H}_6\text{N}_4\text{O}_4\text{B}_2\text{F}_4$ (428.55): Calcd. C, 33.63; H, 1.88; N, 13.07; F, 17.73%. Found C, 33.99; H, 1.92; N, 13.16; F, 17.36%. IR (ν): 1610 cm^{-1} (C=N), UV Vis spectrum (CH_3CN): λ_{max} 448 nm, MS POS FAB (NBA/ CH_3CN) = 428 corresponding to M^+ , POS FAB exact mass = 429.0099 which is consistent with $\text{NiC}_{12}\text{H}_6\text{N}_4\text{O}_4\text{B}_2\text{F}_4$ $[\text{M} + 1]^+$. $^1\text{H-NMR}$ (CD_3CN): δ 6.96 (4H, dd, $J = 7.6 \text{ Hz}/2.8 \text{ Hz}$), 7.13 (4H, dd, $J = 7.6 \text{ Hz}/2.8 \text{ Hz}$). $^{13}\text{C-NMR}$: δ 117.9; 135.7; 136.0.

Preparation of chloro(pyridine) bis (3,5-cyclohexadiene-1,2-dione dioximate) cobalt (III) $[\text{Co}(\text{bqd})_2(\text{py})\text{Cl}]$ (6)

To 2.22 g (16 mmol) of bqdH (3) dissolved in hot 95% ethanol (120 ml) was added 1.9 g (8 mmol)

cobalt chloride hexahydrate in 95% ethanol (50 ml) and the reaction mixture was heated with stirring for about 10 min. Then 1.27 g (16 mmol) pyridine in 95% ethanol (10 ml) was added gradually and the mixture was kept under stirring and heating for 30 min. The reaction mixture was then cooled to room temperature and a stream of air was then allowed to agitate the mixture for 1h. The mixture was kept for few hours after which the product crystallized out of the solution. This was filtered off, washed with little ethanol and dried in vacuo. Yield 2.96 g (83%), m.p. > 300°C. Analysis for $\text{CoC}_{17}\text{H}_{15}\text{N}_5\text{O}_4\text{Cl}$ (447.73): Calcd. C 45.61; H, 3.38; N, 15.64; Cl, 7.92%. Found C, 45.18; H, 3.02; N, 16.04; Cl, 7.72%. IR (ν): 1595 cm^{-1} (C=N), UV-Vis spectrum (THF): λ_{max} 406 nm, MS POS FAB (NBA, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$) = 448 corresponding to $[\text{M} + 1]^+$; exact mass = 448.0223 and these are consistent with $\text{CoC}_{17}\text{H}_{16}\text{N}_5\text{O}_4\text{Cl}$.

Preparation of fluoro (pyridine)-[1,1,8,8-tetrafluoro-4,5,11,12-di(1',3'-butadiene)-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-1,8-dibora-cyclotetradeca-3,5,10,12-tetraene] cobalt(III) $[\text{Co}(\text{bqdBF}_2)_2(\text{py})\text{F}]$ (7)

1.12 g (2.5 mmol) of $[\text{Co}(\text{bqd})_2(\text{py})\text{Cl}]$ (6) was added to 100 ml of freshly distilled acetonitrile and the resulting suspension was brought to reflux under an atmosphere of nitrogen. To this suspension 1.5 ml (12 mmol) boron trifluoride etherate was added slowly with stirring which converted the suspension to a deep-red solution within 15 min. The solvent was removed under reduced pressure and the residue was extracted with two 50 ml portions of acetonitrile and evaporated to dryness. Finally the residue was dissolved in 10 ml of acetonitrile and allowed to stand at 0°C for 3h, where upon the product crystallized from solution. This was filtered off and dried in vacuo. Yield: 0.2 g (15%), m.p. > 300°C. Analysis for $\text{CoC}_{17}\text{H}_{13}\text{N}_5\text{O}_4\text{B}_2\text{F}_5$ (526.87): Calcd C, 38.75; H, 2.49; N, 13.29; F, 18.03%. Found C, 38.43; H, 2.56; N, 13.81; F, 18.39%. IR (ν): 1605 cm^{-1} (C=N), MS POS FAB (NBA/ CH_3CN) = 527 corresponding to $[\text{M} + \text{H}]^+$, POS FAB exact mass = 527.0406 which is consistent with $\text{CoC}_{17}\text{H}_{13}\text{N}_5\text{O}_4\text{B}_2\text{F}_5$ $[\text{M} + 1]^+$.

Crystal structure determination of 5

Silver metallic-like needle crystals of 5 were grown as noted in the experimental section. Crystal dimensions: 0.30 x 0.10 x 0.50 mm. Crystal data for

$C_{12}H_3N_4O_4NiB_2F_4$: FW = 428.53, monoclinic, space group C2/c (#15) with $a = 19.000(2)$, $b = 5.452(2)$, $c = 16.357(1)$ Å, $\beta = 119.251(7)^\circ$, $V = 1519.8(2)$ Å³, $Z = 4$, $d_{calc.} = 1.93$ g/cm³, $F(000) = 856.00$. Data collection was made at 23.0°C using Rigaku AFC5R diffractometer operating in the omega scan mode. 1280 independent reflections were measured within the range $\theta = 6.0 - 60.1^\circ$ using graphite monochromated Cu-K α radiation ($\lambda = 1.54178$ Å) and a rotating anode generator. The cell parameters and orientation matrix for the data collection were obtained using the setting angles of 19 carefully centered reflections ($\theta = 12.1-19.1^\circ$). The structure was solved by direct methods using the program SIR 92, [21] and expanded using the Fourier techniques (DIRDIF 94) [20]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares refinement [22] on F^2 . This resulted in R-values : $R_1 = 0.043$ and $wR_2 = 0.052$ for 1018 observed reflections and 140 variable parameters. GOF = 2.43; the maximum and minimum peaks on the final difference Fourier map corresponded to 0.58 and -0.47 e /Å³, respectively. The hydrogen atoms in the structure were found on the difference Fourier map and were refined isotropically.

Acknowledgements

We thank Professor D.H. Busch, University of Kansas, for inviting ASA to his laboratory, where most of this work was done. ASA would like to thank the Hashemite University for financial support.

Supplementary materials

Full tables of positional parameters, interatomic angles and distances, structural factor amplitudes and thermal parameters, and packing diagrams for the crystal structure of (5) are available from (ASA).

References

1. T. Zincke and P. Schwarz, *Justus Liebigs Ann. Chem.*, **28**, 307 (1899).
2. E.C. Ladd and W.P. Ter Horst, *U.S. Patent* **2**, 336, 941 (1943).
3. M.M El-Abadelah, Z.H. Khan and A.A. Anani, *Synthesis*, 146 (1980).
4. F. Paetzold, J.H. Niclass, H.J. Foerster and L. Zoelch, *Ger. Patent (East) DD*: **237**, 665 (1986); through *Chem. Abs.*, **106**, 15974a (1987).
5. F. Paetzold, J.H. Niclass and H.J. Foerster, *J. Prakt. Chem.*, (5-6), 328, 921 (1986).
6. R. Ohme and E. Gruendemann, *Ger. Patent (East) DD*; **122**, 080 (1976); through *Chem. Abstr.*, **87**, P 134482p (1977).
7. C.L. Pedersen, *Acta Chem. Scand.*, **B30** (7) 675 (1976).
8. a. I. Leichert and J. Weiss, *B31*, 2709, 2877 (1975).
b. H. Endres, H.J. Keller, W. Moroni and J. Weiss, *Acta Cryst.*, **B31**, 2357 (1975).
C. H. Endres, M. Megnamisi-Belombe, H.J. Keller and J. Weiss, *Acta Cryst.*, **B32**, 457 (1976).
9. M. Megnamisi - Belombe, *Ann. N.Y. Acad. Sci.*, **313**, 633 (1978).
10. M. Megnamisi - Belombe, *J. Solid State Chem.*, **22**, 151 (1977).
11. J.W. Brill, M. Magnamisi-Belombe and M. Novotny, *J. Chem. Phys.*, **68**, 585 (1978).
12. F. Pomposo and D.V. Stynes, *Inorg. Chem.*, **22**, 569 (1983).
13. N. Siddiqui and D.V. Stynes, *Inorg. Chem.*, **25**, 1982 (1986).
14. D.W. Thompson and D.V. Stynes, *Inorg. Chem.*, **29**, 3815 (1990).
15. G.N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).
16. G.N. Schrauzer, *Inorg. Synth.*, **11**, 61 (1968).
17. A.S. Abushamleh, P.J. Chmielewski, P.R. Warburton, L. Morales, N.A. Stephenson and D.H. Busch, *J. Coord. Chem.*, **23**, 91 (1991).
18. K.A. Lance, K.A. Goldsby and D.H. Busch, *Inorg. Chem.*, **29**, 4537 (1990).
19. A. Bakac and J.H. Espenson, *J. Am. Chem. Soc.*, **106**, 5197 (1984).
20. L. Tsugaev, *Chem. Ber.*, **40**, 3498 (1907).
21. A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.*, **26**, 343 (1993).
22. P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder R. Israel and J.M.M. Smits (1994). The DIRDIF 94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.