# Crystal structure of *catena*-($\mu_2$-chromato-*O*,*O'*)-3,10-bis-*n*-propyl-1,3,5,8,10,12-hexaazacyclo-tetradecane-nickel(II) tetrahydrate, $Ni(C_{14}H_{34}N_6)(CrO_4) \cdot 4H_2O$

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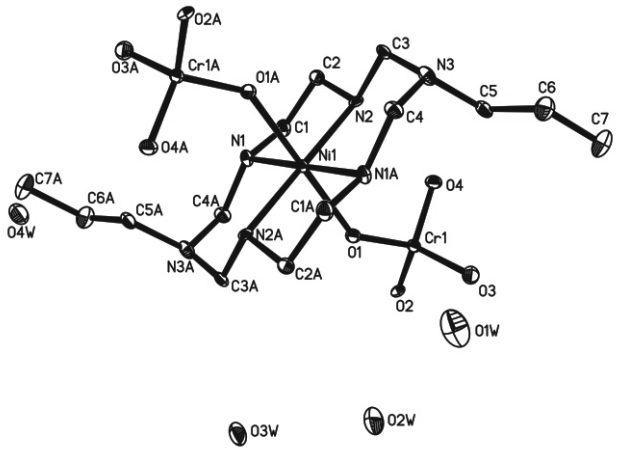


**Abstract**

$C_{14}H_{42}CrN_6NiO_8$, triclinic, $P\bar{1}$ (no. 2), $a$ = 10.507(3) Å, $b$ = 10.720(3) Å, $c$ = 12.222(4) Å, $\alpha$ = 89.232(6)°, $\beta$ = 70.670(6)°, $\gamma$ = 69.433(5)°, $V$ = 1207.9 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.136, $T$ = 173 K.

**Source of material**

A glass tube was charged with the solution of $K_2CrO_4$ (0.019 g, 0.1 mmol) in water (20 mL), and a mixture of methanol and $H_2O$ (1:1, 20 mL) was gently added as an upper layer. A solution of $NiL(ClO_4)_2$ (0.054 g, 0.1 mmol) (L = 3,10-bis-*n*-propyl-1,3,5,8,10,12-hexaazacyclo-tetradecane) in methanol (20 mL) was added carefully as a third layer before the tube was sealed. After a few days, brown crystals were separated in a 28% yield. Elemental analysis — found: C, 31.40 %; H, 8.05 %; N, 15.97 %; calculated for $C_{14}H_{42}CrN_6NiO_8$: C, 31.54 %; H, 7.94 %; N, 15.76 %. IR data are available in the CIF file.

**Discussion**

The macrocyclic nickel(II) complexes with various bridging groups are a subject of great interest because of their importance as potential catalysts as models in the field of metalloproteins. Some multinuclear complexes with chromate as the bridging group have been magnetically and structurally characterized [1,2].

X-ray crystal structural analysis reveals that the title complex contains cations $[NiL]^{2+}$, anions $[CrO_4]^{2-}$, and free water molecules in a ratio 1:1:4. Each Ni(II) ion lies on an inversion center and is coordinated by four macrocyclic nitrogen atoms of L in the equatorial plane and two oxygen atoms of $[CrO_4]^{2-}$ anions in axial positions. Each $[CrO_4]^{2-}$ anion bridges two adjacent $[NiL]^{2+}$ to form a chain. The chains are further connected via hydrogen bonding interactions between the secondary amines of $[NiL]^{2+}$, the oxygen atoms of $[CrO_4]^{2-}$ and free water molecules, generating a three-dimensional supramolecular structure.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | brown prism, size 0.12 × 0.15 × 0.42 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 12.77 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker SMART 1000 CCD, $\varphi/\omega$ |
| $2\theta_{max}$: | 50° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 7339, 4122 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 2938 |
| $N(param)_{refined}$: | 276 |
| Programs: | SHELXS-97, SHELXL-97, SHELXTL [3] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1A) | 2*i* | 0.1055 | 0.1458 | 0.3796 | 0.026 |
| H(1B) | 2*i* | 0.1304 | 0.2636 | 0.3030 | 0.026 |
| H(2A) | 2*i* | –0.1127 | 0.2802 | 0.3498 | 0.025 |
| H(2B) | 2*i* | –0.1354 | 0.2886 | 0.4864 | 0.025 |
| H(3A) | 2*i* | –0.3288 | 0.5113 | 0.4230 | 0.022 |
| H(3B) | 2*i* | –0.3125 | 0.5117 | 0.5484 | 0.022 |
| H(4A) | 2*i* | –0.3130 | 0.7075 | 0.6368 | 0.024 |
| H(4B) | 2*i* | –0.3229 | 0.8377 | 0.5698 | 0.024 |
| H(5A) | 2*i* | –0.2962 | 0.6765 | 0.3056 | 0.025 |
| H(5B) | 2*i* | –0.1791 | 0.7229 | 0.3320 | 0.025 |
| H(6A) | 2*i* | –0.3622 | 0.9328 | 0.4213 | 0.038 |
| H(6B) | 2*i* | –0.4790 | 0.8864 | 0.3944 | 0.038 |
| H(7A) | 2*i* | –0.2384 | 0.9212 | 0.2191 | 0.060 |
| H(7B) | 2*i* | –0.4039 | 1.0200 | 0.2520 | 0.060 |
| H(7C) | 2*i* | –0.3518 | 0.8709 | 0.1908 | 0.060 |
| H(8A) | 2*i* | 0.3641 | 0.8604 | 0.1204 | 0.027 |
| H(8B) | 2*i* | 0.5287 | 0.7744 | 0.0406 | 0.027 |
| H(9A) | 2*i* | 0.4908 | 0.7226 | 0.2365 | 0.025 |
| H(9B) | 2*i* | 0.3576 | 0.6814 | 0.2372 | 0.025 |
| H(10A) | 2*i* | 0.5796 | 0.4749 | 0.2850 | 0.027 |
| H(10B) | 2*i* | 0.4539 | 0.4472 | 0.2556 | 0.027 |
| H(11A) | 2*i* | 0.8215 | 0.3558 | 0.1784 | 0.026 |
| H(11B) | 2*i* | 0.8313 | 0.3207 | 0.0484 | 0.026 |
| H(12A) | 2*i* | 0.8799 | 0.1230 | 0.2057 | 0.038 |
| H(12B) | 2*i* | 0.8967 | 0.0902 | 0.0732 | 0.038 |
| H(13A) | 2*i* | 1.0957 | 0.1568 | 0.0058 | 0.056 |
| H(13B) | 2*i* | 1.1251 | 0.0469 | 0.0935 | 0.056 |
| H(13C) | 2*i* | 1.0751 | 0.2025 | 0.1366 | 0.056 |

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**Table 2.** Continued.

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(14A) | 2*i* | 0.3291 | 0.8531 | –0.0816 | 0.026 |
| H(14B) | 2*i* | 0.4924 | 0.7497 | –0.1384 | 0.026 |
| H(1C) | 2*i* | 0.0855 | 0.2594 | 0.5387 | 0.022 |
| H(2C) | 2*i* | –0.0899 | 0.4787 | 0.3387 | 0.017 |
| H(4C) | 2*i* | 0.2855 | 0.7177 | 0.0570 | 0.022 |
| H(5C) | 2*i* | 0.6476 | 0.5477 | 0.1061 | 0.020 |
| H(1E) | 2*i* | 0.0854 | 0.8469 | 0.2944 | 0.098 |

**Table 2.** Continued.

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1D) | 2*i* | –0.0199 | 0.9293 | 0.3933 | 0.098 |
| H(2E) | 2*i* | 0.1906 | 0.9202 | 0.4419 | 0.076 |
| H(2D) | 2*i* | 0.2545 | 0.8927 | 0.5269 | 0.076 |
| H(3C) | 2*i* | 0.4723 | 0.7320 | 0.5500 | 0.051 |
| H(3D) | 2*i* | 0.3657 | 0.7589 | 0.6600 | 0.051 |
| H(4E) | 2*i* | 0.1149 | 0.4321 | 0.9022 | 0.044 |
| H(4D) | 2*i* | 0.1462 | 0.3846 | 1.0004 | 0.044 |

**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| C(1) | 2*i* | 0.0783(5) | 0.2442(4) | 0.3809(4) | 0.026(3) | 0.021(2) | 0.021(3) | –0.008(2) | –0.011(2) | 0.003(2) |
| C(2) | 2*i* | –0.0834(5) | 0.3115(4) | 0.4101(4) | 0.026(3) | 0.023(2) | 0.023(3) | –0.015(2) | –0.015(2) | 0.007(2) |
| C(3) | 2*i* | –0.2774(4) | 0.5364(4) | 0.4687(4) | 0.014(2) | 0.029(2) | 0.017(3) | –0.010(2) | –0.010(2) | 0.005(2) |
| C(4) | 2*i* | –0.2753(4) | 0.7388(4) | 0.5604(4) | 0.014(2) | 0.028(2) | 0.016(3) | –0.005(2) | –0.002(2) | –0.001(2) |
| C(5) | 2*i* | –0.2823(5) | 0.7323(4) | 0.3613(4) | 0.015(2) | 0.032(2) | 0.018(3) | –0.007(2) | –0.008(2) | 0.002(2) |
| C(6) | 2*i* | –0.3758(6) | 0.8768(5) | 0.3656(4) | 0.037(3) | 0.030(3) | 0.025(3) | –0.010(2) | –0.010(3) | 0.005(2) |
| C(7) | 2*i* | –0.3392(6) | 0.9267(5) | 0.2463(5) | 0.057(4) | 0.033(3) | 0.030(3) | –0.017(3) | –0.015(3) | 0.014(2) |
| C(8) | 2*i* | 0.4348(5) | 0.7685(4) | 0.0882(4) | 0.022(2) | 0.023(2) | 0.024(3) | –0.010(2) | –0.010(2) | 0.002(2) |
| C(9) | 2*i* | 0.4527(5) | 0.6834(4) | 0.1874(4) | 0.020(2) | 0.025(2) | 0.019(3) | –0.006(2) | –0.010(2) | –0.005(2) |
| C(10) | 2*i* | 0.5537(5) | 0.4467(4) | 0.2210(4) | 0.024(3) | 0.030(2) | 0.012(3) | –0.007(2) | –0.009(2) | –0.001(2) |
| C(11) | 2*i* | 0.8063(5) | 0.2945(4) | 0.1285(4) | 0.024(3) | 0.031(2) | 0.017(3) | –0.014(2) | –0.011(2) | 0.007(2) |
| C(12) | 2*i* | 0.9078(5) | 0.1511(5) | 0.1265(5) | 0.026(3) | 0.032(3) | 0.036(3) | –0.009(2) | –0.010(2) | –0.004(2) |
| C(13) | 2*i* | 1.0647(5) | 0.1382(5) | 0.0871(5) | 0.028(3) | 0.036(3) | 0.041(4) | –0.006(2) | –0.010(3) | –0.005(3) |
| C(14) | 2*i* | 0.3913(5) | 0.7567(4) | –0.0968(4) | 0.024(3) | 0.024(2) | 0.021(3) | –0.012(2) | –0.011(2) | 0.010(2) |
| Cr(1) | 2*i* | 0.14928(7) | 0.54891(6) | 0.20274(6) | 0.0140(4) | 0.0243(4) | 0.0122(4) | –0.0089(3) | –0.0053(3) | 0.0044(3) |
| N(1) | 2*i* | 0.1180(4) | 0.2961(3) | 0.4704(3) | 0.020(2) | 0.020(2) | 0.017(2) | –0.006(2) | –0.011(2) | 0.003(2) |
| N(2) | 2*i* | –0.1208(4) | 0.4580(3) | 0.4148(3) | 0.015(2) | 0.021(2) | 0.009(2) | –0.012(2) | –0.002(2) | 0.005(2) |
| N(3) | 2*i* | –0.3158(4) | 0.6825(3) | 0.4759(3) | 0.018(2) | 0.027(2) | 0.016(2) | –0.004(2) | –0.009(2) | –0.004(2) |
| N(4) | 2*i* | 0.3823(4) | 0.7032(3) | 0.0157(3) | 0.018(2) | 0.023(2) | 0.019(2) | –0.011(2) | –0.009(2) | 0.004(2) |
| N(5) | 2*i* | 0.5545(4) | 0.5463(3) | 0.1362(3) | 0.015(2) | 0.023(2) | 0.015(2) | –0.008(2) | –0.008(2) | 0.004(2) |
| N(6) | 2*i* | 0.6520(4) | 0.3102(3) | 0.1725(3) | 0.018(2) | 0.023(2) | 0.017(2) | –0.010(2) | –0.008(2) | 0.009(2) |
| Ni(1) | 1*g* | 0 | ½ | ½ | 0.0137(4) | 0.0202(4) | 0.0116(4) | –0.0083(3) | –0.0064(3) | 0.0039(3) |
| Ni(2) | 1*e* | ½ | ½ | 0 | 0.0135(4) | 0.0198(4) | 0.0117(4) | –0.0070(3) | –0.0055(3) | 0.0042(3) |
| O(1) | 2*i* | 0.1370(3) | 0.5293(3) | 0.3400(3) | 0.021(2) | 0.037(2) | 0.015(2) | –0.017(1) | –0.009(1) | 0.010(1) |
| O(2) | 2*i* | 0.3182(3) | 0.4693(3) | 0.1147(3) | 0.016(2) | 0.023(2) | 0.016(2) | –0.011(1) | –0.003(1) | 0.008(1) |
| O(3) | 2*i* | 0.1025(3) | 0.7091(3) | 0.1857(3) | 0.021(2) | 0.025(2) | 0.023(2) | –0.007(1) | –0.006(2) | 0.004(1) |
| O(4) | 2*i* | 0.0401(3) | 0.4879(3) | 0.1709(3) | 0.019(2) | 0.033(2) | 0.018(2) | –0.014(1) | –0.006(1) | 0.005(1) |
| O(1W) | 2*i* | 0.0719(5) | 0.8975(4) | 0.3547(4) | 0.075(3) | 0.052(3) | 0.064(3) | –0.002(2) | –0.040(3) | –0.016(2) |
| O(2W) | 2*i* | 0.2049(4) | 0.9561(3) | 0.4969(4) | 0.051(3) | 0.043(2) | 0.076(3) | –0.017(2) | –0.044(2) | 0.029(2) |
| O(3W) | 2*i* | 0.3799(3) | 0.7582(3) | 0.5865(3) | 0.018(2) | 0.054(2) | 0.029(2) | –0.010(2) | –0.012(2) | 0.017(2) |
| O(4W) | 2*i* | 0.1831(3) | 0.3866(3) | 0.9266(3) | 0.025(2) | 0.040(2) | 0.025(2) | –0.011(2) | –0.012(2) | 0.003(2) |

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## References

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