

Cs₂NiO₂ Revisited. Crystal Structure and Magnetic Properties

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Single crystals as well as microcrystalline powders of Cs₂NiO₂ were obtained *via* the azide/nitrate route from appropriate mixtures of CsN₃, CsNO₃ and NiO. The single-crystal structure analysis confirmed that Cs₂NiO₂ crystallizes in the tetragonal space group *I4/mmm* (*Z* = 2, *a* = 4.4090(3), *c* = 13.576(3) Å, *R*1 = 0.036, *wR*2 = 0.093). Above 45 K, Cs₂NiO₂ is paramagnetic, and an analysis based on the Curie-Weiss law has resulted in $\mu = 2.89 \mu_B$ paramagnetic units, $\theta = -30.8$ K and $T_N \sim 20$ K.

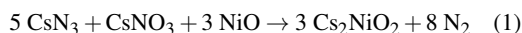
Key words: High-spin Nickel(II) Compounds, Linear Coordination, Antiferromagnetic Ordering, Azide/Nitrate Route

Introduction

Linear coordination geometries constitute a characteristic structural feature in the chemistry of species with $nd^{10}(n+1)s^0(n+1)p^0$ electron configuration. Surprisingly, linear $[X-M-X]_m^{n-}$ anions are also quite common for Fe, Co and Ni in low oxidation states, obviously independent of the respective valence electron counts. Among them is the family of nickelates(II), K₂NiO₂, Rb₂NiO₂ and Cs₂NiO₂, as discovered by H. Rieck and R. Hoppe [1, 2]. While the potassium and rubidium representatives have been well characterized and reinvestigated with respect to their magnetic and optical properties [3, 4], knowledge about Cs₂NiO₂ has remained rudimentary. Here we report on the growth of single-crystals and a structure determination from single-crystal data, as well as on the magnetic properties of a single-phase sample.

Experimental Section

Starting materials for the preparation of dicaesium nickelate(II) were caesium azide, caesium nitrate (Riedel-De Haën AG Seelze Hannover 99.5 %) and NiO, prepared by decomposition of Ni(C₂O₄) · 0.5H₂O (Alfa Aesar, 98 %) in a flow of oxygen at 623 K for 20 h. The caesium azide was synthesised from aqueous HN₃ and CsCO₃ (Sigma Aldrich, 99 %). The starting compounds were dried under vacuum (10⁻³ mbar) at 393 K over night, mixed and thoroughly ground in an agate mortar in a glove box, and placed under argon in a tightly closed steel container, provided with a silver inlay [5].



Single crystals of the title compound were obtained when an excess of azide and nitrate as compared to Eq. 1 was used (30 mol-% excess for CsN₃ and 150 mol-% excess for CsNO₃) and the mixture heated with the following temperature program: 298 → 533 K (100 K h⁻¹), 533 → 653 K (5 K h⁻¹), 653 → 723 K (20 K h⁻¹), with a subsequent annealing for 100 h at 723 K. Green microcrystalline samples of Cs₂NiO₂ were obtained from stoichiometric mixtures of the reactants according to Eq. 1, and applying the following temperature treatment: 298 → 533 K (100 K h⁻¹), 533 → 653 K (5 K h⁻¹), 653 → 773 K (20 K h⁻¹) and subsequent annealing for 30 h at 773 K.

Hazards: In order to carry out the reaction in a controlled manner, specially designed containers have to be used (with no welded seals), and a slow heating regime in the 533 → 653 K temperature range must be applied.

The obtained powders as well as the single crystals are very sensitive towards air and moisture. Therefore they were sealed in glass ampoules under argon atmosphere, and all further manipulations were made in an inert atmosphere of purified argon.

Powder X-ray patterns were collected with a linear position-sensitive detector on a STADIP diffractometer in Debye-Scherrer geometry (Stoe & Cie GmbH, Germany, Ge(111)-monochromatized MoK_{α1} radiation, $\lambda = 0.7093$ Å, $4 < 2\theta < 40^\circ$, in steps of 0.01°), with the samples sealed in glass capillaries of 0.3 mm diameter. The data were calibrated with respect to an external Si standard. Structure parameters were calculated and refined from the powder X-ray patterns using TOPAS-ACADEMIC software [6].

The single-crystal measurements were carried out on a Stoe IPDS-II diffractometer with graphite-monochromatized MoK_α radiation at r. t. ($\lambda = 0.71073$ Å). Intensities

Table 1. Single-crystal structure data for Cs₂NiO₂.

M_r	356.53
Crystal size, mm ³	0.25 × 0.10 × 0.11
Crystal system	tetragonal
Space group	$I4/mmm$ (no. 139)
a , Å	4.4090(6)
c , Å	13.576(3)
V , Å ³	263.91(7)
Z	2
D_{calcd} , g cm ⁻³	4.49
$\mu(\text{MoK}\alpha)$, mm ⁻¹	17.1
$F(000)$, e	308
hkl range	±6, ±6, ±20
$((\sin \theta)/\lambda)_{\text{max}}$, Å ⁻¹	0.737
Refl. measured / unique / R_{int}	2922 / 158 / 0.0743
Param. refined	10
$R1(F) / wR2(F^2)^{a,b}$ (all refl.)	0.0364 / 0.0930
GoF (F^2) ^c	1.459
$\Delta\rho_{\text{fin}}$ (max / min), e Å ⁻³	2.26 / -1.82

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0516P)^2 + 0.5355P]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$; ^c $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

were corrected numerically for absorption effects [7]. The structure was solved by Direct Methods and refined by full-matrix least-squares fitting with SHELXTL [8].

Thermal analyses were carried out using a TG/DTA device (STA 409, Netzsch) coupled with a quadrupole mass spectrometer (QMG 421, Balzers). The samples were heated at a rate of 10 K min⁻¹ in a corundum crucible, under dry argon.

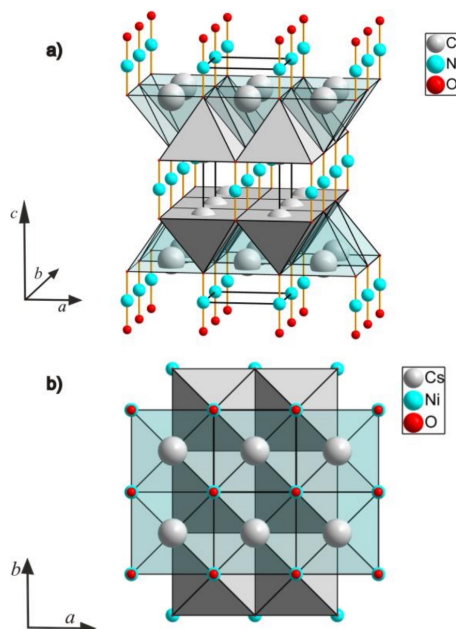
The magnetic susceptibility was measured in the temperature range from 2 to 400 K, in magnetic fields up to 7 T using a SQUID magnetometer (MPMS 5.5, Quantum Design). Diamagnetic correction was applied according to tabulated values [9], and a Honda-Owen correction ($1/H \rightarrow 0$) to correct for traces of ferromagnetic impurities.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-423923.

Results and Discussion

Single crystals as well as microcrystalline powders of Cs₂NiO₂ were synthesized along the azide nitrate route. According to thermal analysis its decomposition starts close to 923 K, above ~ 1073 K NiO is left as the only solid residue.

The crystal structure determinations and refinements were performed on single-crystal X-ray data collected at 298 K. Details of the solution are given

Fig. 1 (color online). Crystal structure of Cs₂NiO₂.

in Tables 1 and 2. Single crystal refinement has revealed that Cs₂NiO₂ crystallizes in the tetragonal space group $I4/mmm$ ($Z = 2$, $a = 4.4090(6)$, $c = 13.576(3)$ Å), which is in good agreement with the previously published results obtained from powder data [1].

Cs₂NiO₂ is isostructural to A₂NiO₂ ($A = \text{K, Rb}$) and can be regarded as a stuffed XeF₂ structure. The green color originates from the unusual linear NiO₂²⁻ units ($d(\text{Ni}-\text{O}) = 1.68$ Å, Fig. 1). The Cs ion is surrounded by five oxygen atoms, forming a tetragonal pyramid. Adjacent CsO₅ pyramids are connected through their basal edges, which leads to the formation of infinite $\infty^2\text{CsO}$ double sheets. Each of these oxygen atoms is thus common to four pyramids in a $\infty^2\text{CsO}$ sheet, and at the same time they are positioned above those of the pyramids of the adjacent sheet (Fig. 1b). Interconnection between these double layers is realized *via* NiO₂²⁻ units, whose oxygen atoms occupy the apical positions of the CsO₅ pyramids.

K₂NiO₂, Rb₂NiO₂ and Cs₂NiO₂ display identical Ni–O distances (within the margins of experimental error, Table 3). However, with increasing size of the A cations in A₂NiO₂ ($A = \text{K, Rb, Cs}$) and the increasing size of the unit cell, the Ni–Ni distances are also growing, with the consequence that the Néel temperature within this family of compounds is expected to be lowest for Cs₂NiO₂.

Atom	Site	x	y	z	U_{eq}	U_{11}	U_{33}
Cs	4e	0	0	0.3478(1)	0.0316(6)	0.0318(6)	0.0310(7)
Ni	2a	0	0	0	0.0247(6)	0.0245(6)	0.025(1)
O	4e	0	0	0.1242(9)	0.044(2)	0.045(3)	0.041(6)

Table 2. Atomic coordinates and anisotropic displacement parameters (\AA^2) for Cs₂NiO₂ ($U_{11} = U_{22}$, $U_{12} = U_{13} = U_{23} = 0$).

Table 3. Lattice parameters and interatomic distances (\AA) in A₂NiO₂ (A = K, Rb, Cs) compounds.

	K ₂ NiO ₂ [1]	Rb ₂ NiO ₂ [2]	Cs ₂ NiO ₂
<i>a</i>	3.953	4.166(1)	4.4069(3) ^a
<i>c</i>	12.853	13.146(2)	13.561(1) ^a
<i>d</i> (Ni–O)	1.68	1.67	1.68
<i>d</i> (A–O)	2.72	2.87	3.03
<i>d</i> (A–O)	2.82	2.97	3.14

^a Lattice constants refined from the powder data.

Table 4. Crystallographic data for Cs₂NiO₂ as obtained by Rietveld refinement (tetragonal space group *I4/mmm*, *Z* = 2).

Temperature, K	298
Lattice constants	
<i>a</i> , \AA	4.4069(3)
<i>c</i> , \AA	13.561(1)
<i>V</i> , \AA^3	263.37(4)
<i>D</i> _{calcd} , g cm ⁻³	4.49
Radiation; monochromator; λ , \AA	MoK α 1; Ge(111); 0.7093
2 θ range data collection, deg	5–40
<i>R</i> _{Bragg} (%)	2.02
<i>R</i> _p (%)	7.46
<i>R</i> _{wp} (%)	9.56

In order to investigate the magnetic properties of Cs₂NiO₂, phase-pure microcrystalline powder was synthesized. The phase purity of the powder was analyzed with the Rietveld method, according to which the only second phase noticeable was silver in traces ($\sim 1\%$), from the silver inlay. Rietveld plots of the refinement are shown in Fig. 2, parameters related to the Rietveld refinements are given in Table 4.

The magnetic susceptibility of Cs₂NiO₂ was examined at different magnetic fields (1, 3, 5 and 7 T). The paramagnetic branch can be fitted using the Curie-Weiss law (Fig. 3), where Cs₂NiO₂ orders antiferromagnetically at 20 K. Ni–Ni distances are surprisingly large (Table 3) ruling out direct interactions. A weak magnetic field dependency indicates the presence of small ferromagnetic impurities. Assuming a saturation of the magnetization of the ferromagnetic impurities, a correction was made by plotting χ against $1/H$ and extrapolating linearly to $1/H = 0$ (Honda-Owen plot). An effective magnetic moment of $\mu = 2.89 \mu_B$ paramagnetic units ($\theta = -30.8$ K) was derived from the measurement in the highest magnetic field, which is in good agreement with a magnetic moment as expected for a d^8 free ion [8], including a slight orbital

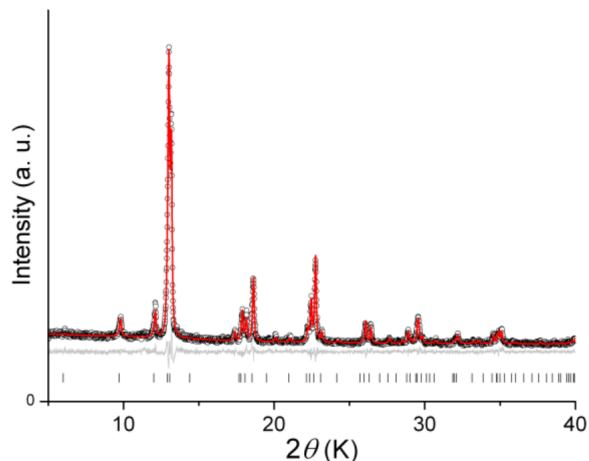


Fig. 2 (color online). Experimental and calculated XRD pattern for Cs₂NiO₂; black marks: experimental, red: calculated profile. The difference between the experimental and theoretical pattern is given in gray. Bragg positions are given by thick marks.

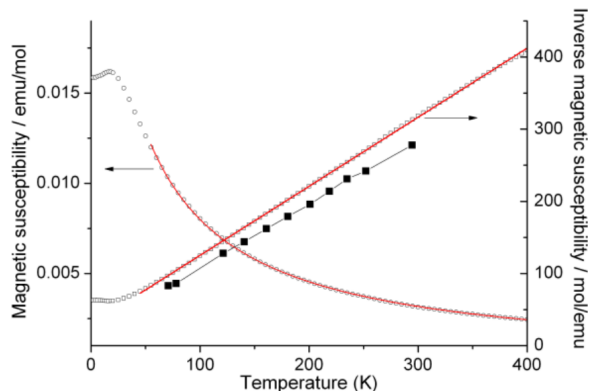


Fig. 3 (color online). Magnetic susceptibility and inverse magnetic susceptibility of Cs₂NiO₂, corrected for diamagnetic contributions of the closed electronic shells and for traces of ferromagnetic impurities by the Honda-Owen extrapolation. The black squares (■) correspond to the magnetic data of Cs₂NiO₂ as reported by Rieck and Hoppe [1].

contribution, as well as with the magnetic susceptibility data obtained by Rieck and Hoppe [1]. However, the previously published data only cover the ~ 70 – 300 K temperature range. Among the other members of the A₂NiO₂ family, only for Rb₂NiO₂ low-temperature magnetic susceptibility data are available.

As a striking, still unresolved discrepancy with our result, no antiferromagnetic ordering for Rb₂NiO₂ was observed [4].

Conclusion

Single-crystals as well as phase-pure powders of Cs₂NiO₂ were synthesised for the first time along the azide nitrate route. Cs₂NiO₂ is paramagnetic in the

high-temperature range and orders antiferromagnetically at 20 K.

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