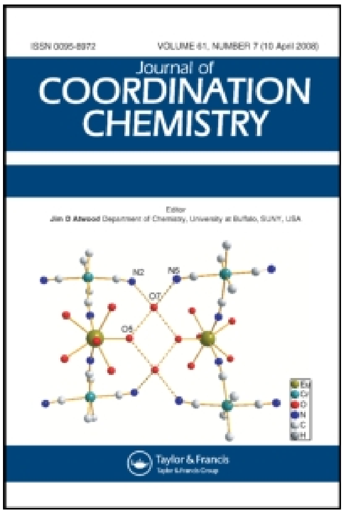

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal and Molecular Structure of Potassium *trans*-bis(iminodiacetato)-cobaltate(III)-$2H_2O$

Peter C. Junk[a]; Matthew K. Smith[b]
[a] School of Chemistry, Monash University, Clayton, Victoria, Australia [b] Department of Chemistry, James Cook University, Townsville, Qld, Australia

To cite this Article Junk, Peter C. and Smith, Matthew K.(2002) 'Crystal and Molecular Structure of Potassium *trans*-bis(iminodiacetato)-cobaltate(III)-$2H_2O$', Journal of Coordination Chemistry, 55: 9, 1091 — 1096
To link to this Article: DOI: 10.1080/0095897021000010044
URL: http://dx.doi.org/10.1080/0095897021000010044

J. Coord. Chem., 2002, Vol. 55(9), pp. 1091–1096

Taylor & Francis
Taylor & Francis Group

CRYSTAL AND MOLECULAR STRUCTURE OF POTASSIUM *TRANS*-BIS(IMINODIACETATO)-COBALTATE(III)-$2H_2O$

PETER C. JUNK[a,]* and MATTHEW K. SMITH[b]

[a]*School of Chemistry, Box 23, Monash University, Clayton, Victoria 3800, Australia;*
[b]*Department of Chemistry, James Cook University, Townsville, Qld 4811, Australia*

(Received 24 August 2001; Revised 23 October 2001; In final form 1 March 2002)

The combination of iminodiacetic acid (H_2ida) with cobalt(II) chloride hexahydrate in the presence of sodium hydroxide, followed by heating, produces the *trans*-facial isomer of $K[Co(ida)_2]\cdot 2H_2O$. This compound contains extensive intermolecular and intramolecular coordination and hydrogen bonding involving the potassium ions, and results in a complex three-dimensional structure in which each potassium ion is immediately surrounded by six cobalt centers.

Keywords: Cobalt (III); Iminodiacetic acid; Potassium; Crystal structure

INTRODUCTION

The coordination chemistry of cobalt(II) and (III) with multidentate ligands has been comprehensively studied [1] and indeed the history of coordination chemistry has its origins in the chemistry of cobalt [2,3]. Bis(imidodiacetate) complexes of cobalt(III) have been known for some time. Two isomers, the violet *cis*-$K[Co(ida)_2]$ [3,4] (ida = imidoacetate) and the brown *trans*-$K[Co(ida)_2]$ [4] were originally assigned by comparison of the visible spectra of these with known complexes but both of these have since been fully characterized (with only the *cis* isomer being characterized by x-ray crystallography) [6]. In both examples, the ida ligands favor the facial conformation, and will only bind in a meridional fashion if forced to do so [7]. The x-ray crystal structure of the violet *cis* isomer of $K[Co(ida)_2]\cdot 2H_2O$ was reported nearly 30 years ago [5] and since then, only two reports of x-ray crystal structures of the *trans* isomer of cobalt(III) have appeared in the literature; *viz* Ca[*trans*-$Co(ida)_2]_2\cdot 6H_2O$ [8] and (H_5O_2)[*trans*-$Co(ida)_2]\cdot 2H_2O$ [9], while the x-ray structure of cobalt(II) complex $Na_2[Co(ida)_2]\cdot 7H_2O$ has also been performed. [10] The structure of the potassium salt has still not been published and we therefore report here the x-ray crystal structure of the *trans*-N facial isomer of $K[Co(ida)_2]\cdot 2H_2O$.

---

*Corresponding author. Tel. 03 9905 4570. Fax: 03 9905 4570. E-mail: peter.junk@sci.monash.edu.au

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000010044

EXPERIMENTAL

The *trans*-N facial isomer of $K[Co(ida)_2]\cdot 2H_2O$ was synthesized according to the literature method [4]. Dark brown x-ray quality crystals were isolated by slow cooling of the reaction mixture.

Crystal Structure Determination

A crystal of $K[Co(ida)_2]\cdot 2H_2O$ was mounted on a glass fibre using epoxy resin, and a hemisphere of data were collected at room temperature on a Bruker SMART CCD diffractometer using the omega scan mode with total reflections and unique data listed in Table I. Data were corrected for absorption using the program SADABS. [11]. The position of the heavy atoms were found using the Patterson method and refined on F^2 using SHELXL97-2 [12] with X-SEED [13] as a graphics interface. All non-hydrogen atoms were located and were refined with anisotropic thermal parameters. All hydrogen atoms were located and refined with isotropic thermal parameters. Crystal data and a summary of data collection appear in Table I, while positional parameters and selected bond distances and angles appear in Tables II and III, and hydrogen bonding parameters are compiled in Table IV.

DISCUSSION

$K[Co(ida)_2]\cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with one half of the complex in the asymmetric unit and both potassium and cobalt atoms residing on inversion centers. In the $[Co(ida)_2]^-$ anion, the cobalt center is close to regular octahedral geometry with the two ida ligands being bound in a tridentate fashion through two carboxylato oxygen centers and the imino nitrogen center (Fig. 1). The ligands are bound in a facial arrangement with the nitrogen atoms in *transoid* positions. The cobalt–nitrogen (Co(1)–N(1), 1.931(2) Å) and cobalt–oxygen distances

TABLE I Crystal data and structure refinement for $K[\textit{trans}\text{-}Co(ida)_2]\cdot 2H_2O$

Molecular formula	$C_8H_{14}CoKN_2O_{10}$
Molecular weight	396.24
Crystal system, space group	monoclinic, $P2_1/c$
Cell dimensions	
a (Å)	5.1584(9)
b (Å)	11.2002(19)
c (Å)	12.068(2)
β (°)	97.574(3)
Volume (Å^3)	691.1(2)
Z	2
Calculated density (g cm^{-3})	1.904
Absorption coefficient (mm^{-1})	1.599
$F(000)$	404
Crystal size (mm)	0.50 × 0.50 × 0.40
Reflections collected/unique	3042/997 [R(int) = 0.0558]
Max. and min. transmission	0.5672 and 0.5020
Data/restraints/parameters	997/0/132
Final R indices [$I > 2$ sigma (I)]	$R1 = 0.0435$, $wR2 = 0.1096$
R indices (all data)	$R1 = 0.0460$, $wR2 = 0.1121$

TABLE II Atomic coordinates and isotropic displacement parameters for K[*trans*-Co(ida)$_2$] $\cdot$ 2H$_2$O

	x	*y*	*z*	*U(eq)*
Co(1)	0.5000	0.5000	0.5000	0.024(1)
K(1)	0	0	0.5000	0.062(1)
O(1)	0.2064(4)	0.5299(2)	0.3936(1)	0.033(1)
N(1)	0.6689(4)	0.4414(2)	0.3772(2)	0.029(1)
C(1)	0.2558(5)	0.5323(2)	0.2911(2)	0.028(1)
O(2)	0.0998(3)	0.5705(2)	0.2139(2)	0.039(1)
C(2)	0.5234(7)	0.4882(3)	0.2716(3)	0.033(1)
O(3)	0.3829(3)	0.3422(2)	0.5171(1)	0.036(1)
C(3)	0.6838(6)	0.3100(3)	0.3864(3)	0.041(1)
O(4)	0.4586(5)	0.1543(2)	0.4701(2)	0.062(1)
C(4)	0.4954(6)	0.2618(2)	0.4619(2)	0.039(1)
O(5)	0.0878(7)	0.2126(3)	0.6646(4)	0.087(1)

TABLE III Selected (i) bond lengths [A] and (ii) angles [deg] for K[*trans*-Co(ida)$_2$] $\cdot$ 2H$_2$O

Atoms	*Distance*	*Atoms*	*Distance*
(i)			
Co(1)–O(1)	1.8817(17)	K(1)–O(2)#2	2.6837(18)
Co(1)–O(3)	1.8882(17)	K(1)–O(4)	2.989(2)
Co(1)–N(1)	1.931(2)	K(1)–O(5)	3.096(5)
		K(1)–O(4)#5	3.263(3)
(ii)			
O(1)–Co(1)–O(1)#1	180.0	O(3)–Co(1)–N(1)	87.08(8)
O(1)–Co(1)–O(3)	90.05(8)	O(1)–Co(1)–N(1)#1	93.40(8)
O(1)–Co(1)–O(3)#1	89.95(8)	O(3)–Co(1)–N(1)#1	92.92(8)
O(3)–Co(1)–O(3)#1	180.0	N(1)–Co(1)–N(1)#1	180.0
O(1)–Co(1)–N(1)	86.60(8)	O(2)#2–K(1)–O(2)#3	180.0
O(2)#2–K(1)–O(4)	76.62(7)	O(2)#3–K(1)–O(4)	103.38(7)
O(2)#2–K(1)–O(4)#5	108.36(6)	O(2)#3–K(1)–O(4)#5	71.64(6)
O(2)#2–K(1)–O(5)	112.60(8)	O(2)#3–K(1)–O(5)	67.40(8)
O(4)#4–K(1)–O(4)	180.0	O(4)–K(1)–O(4)#5	68.90(7)
O(4)–K(1)–O(4)#6	111.10(7)	O(4)–K(1)–O(5)#4	114.73(8)
O(4)–K(1)–O(5)	65.27(8)	O(4)#5–K(1)–O(5)	106.60(8)
O(4)#6–K(1)–O(5)	73.40(8)	O(5)#4–K(1)–O(5)	180.0

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$; #2 $-x, y-1/2, -z+1/2$; #3 $x, -y+1/2, z+1/2$; #4 $-x, -y, -z+1$; #5 $-x+1, -y, -z+1$; #6 $x, -1, y, z$.

TABLE IV Hydrogen bonds for K[*trans*-Co(ida)$_2$] $\cdot$ 2H$_2$O [A and deg]

D–H$\cdots$A	*d(D–H)*	*d(H$\cdots$A)*	*d(D$\cdots$A)*	*<(DHA)*
N(1)–H(1)$\cdots$O(1)#8	0.81(4)	2.12(4)	2.926(3)	177(3)
O(5)–H(4)$\cdots$O(2)#9	0.75(7)	2.36(7)	3.060(4)	155(7)
O(5)–H(9)$\cdots$O(3)	0.78(7)	2.12(7)	2.882(4)	167(6)

Symmetry transformations used to generate equivalent atoms: #8 $x+1, y, z$; #9 $-x, -y+1, -z+1$.

(Co(1)–O(1), 1.882(2), Co(1)–O(3), 1.888(2) Å) are unexceptional and similar to those in the *cis* isomer [5]. As in the *cis* isomer, the C–O distances in the ida ligand are asymmetric [5]. Where the oxygen atoms are bound to Co, the C–O distances are longer (C–O, 1.296(3) and 1.301(3) Å) than those that are uncomplexed, (C–O, 1.225(3) and 1.225(4) Å) corresponding to double bond character in the latter. The angles about the cobalt center are close to 90° (Table III) confirming octahedral geometry.

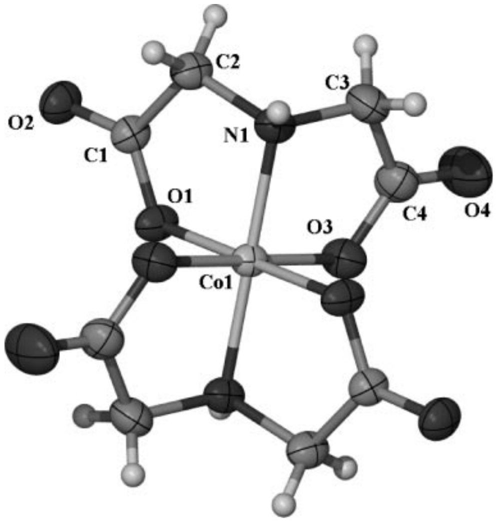

FIGURE 1 The octahedral coordination geometry about cobalt in $K[Co(ida)_2] \cdot 2H_2O$.

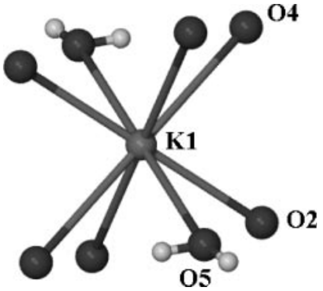

FIGURE 2 The bicapped octahedral geometry about potassium in $K[Co(ida)_2] \cdot 2H_2O$.

The potassium ion does not exist as a discrete ion in the lattice, but rather is coordinated to eight oxygen centers, giving it a geometry most closely described [14] as a bicapped octahedron (Fig. 2). The eight-fold coordination arises from two water molecules and six carbonyl oxygens of the ida ligands, with the water molecules situated in the capping positions of the octahedron (Fig. 2). The K–O distances vary considerably with K(1)–O(2) being 2.684(2) Å and K(1)–O(4) of 3.263(3) Å spanning this range. The K–O(water) distances (3.096(5) Å) are at the upper end of this range.

The interaction between potassium ions and the carbonyl oxygen atoms of the ida ligands result in interesting packing of the crystal lattice (Fig. 3). Each potassium center is surrounded by six $[Co(ida)_2]^-$ anions, which in turn are coordinatively attached to four potassium centers through the carbonyl oxygens of the ida in a second sphere fashion. The cations and anions thus alternate along both the crystallographic *b* and *c* axes. Additionally, the water molecules bound to potassium are hydrogen bound to the nitrogen atom and are involved in an extensive hydrogen bonded array, further holding the lattice in a rigid framework (Table IV, Fig. 3). The potassium ions therefore act as coordination linkers, and effectively connect the entire crystal in a coordinated polymeric array. This packing is similar to that

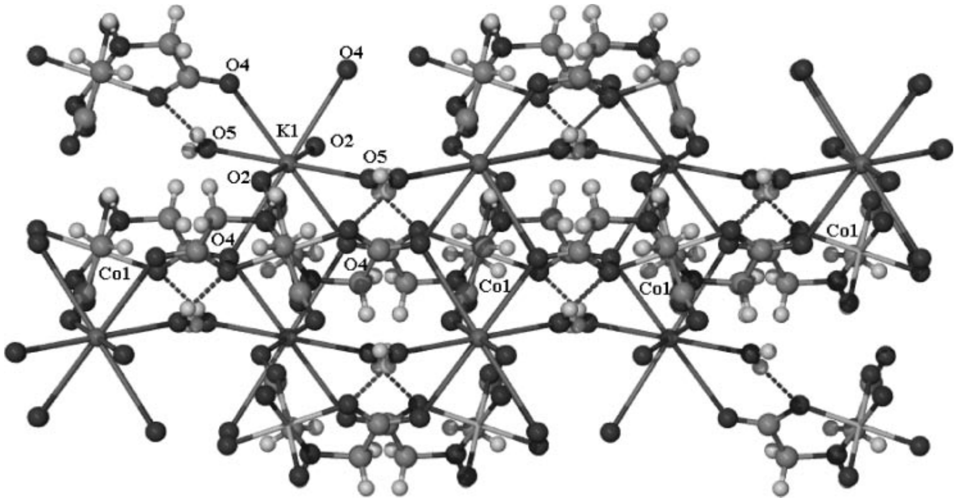

FIGURE 3 Packing diagram of $K[Co(ida)_2] \cdot 2H_2O$ showing the extended three-dimensional structure with extensive hydrogen bonding.

observed in the *cis*-isomer, however the advancement in crystallographic techniques has allowed us to study these packing effects with much greater precision. The structure of the present complex can be compared with Ca[*trans*-$Co(ida)_2]_2 \cdot 6H_2O$ [8] and (H_5O_2)[*trans*-$Co(ida)_2] \cdot 2H_2O$ [9]. The structure of the complex anions in all three cases is essentially identical. However, in comparing the overall three-dimensional structures of the three, distinct differences are observable. In the present complex, *both* the potassium counterions *and* hydrogen bonding contribute to the three dimensional network (see above), while in the calcium complex [8], the calcium atoms link the anions into a two-dimensional layer and hydrogen bonding extends the array to the third dimension. In (H_5O_2)[*trans*-$Co(ida)_2] \cdot 2H_2O$ [9] the overall morphology is a two-dimensional layered structure where hydrogen bonding binds the cations, complex anions and water molecules.

CONCLUSION

The combination of iminodiacetic acid (H_2ida) with cobalt(II) chloride hexahydrate in the presence of sodium hydroxide, followed by heating, results in the formation of the *trans*-facial isomer of the complex $K[Co(ida)_2] \cdot 2H_2O$. Each potassium ion is coordinated to six Co(ida) ions, which in turn act as coordination linkers and cause a highly complex, polymeric packing morphology. The presence of two additional water molecules coordinated to each potassium ion results in intramolecular hydrogen bonding between ida ligands, adding further rigidity to the overall crystal structure.

References

[1] G. Wilkinson, R.D. Gillard and J.A. McCleverty (1987). *Comp. Coord. Chem.* Oxford Press.

[2] (a) A. Werner (1893). *Z. Anorg. Chem*, **3**, 267; (b) A. Werner and A. Miolati (1893). *Z. Phys. Chem.* (*Leipzig*), **12**, 35.

[3] M. Mori, M. Shibid and E. Kyuno (1962). *Bull. Chem. Soc. Japan*, **35**, 75.
[4] J. Hidaka, Y. Shimura and R. Tsuchida (1962). *Bull. Chem. Soc. Japan*, **35**, 567.
[5] A.B. Corradi, C.G. Palmieri, M. Nardelli, M.A. Pellighelli and M.E. Vidoni Tani (1973). *J. Chem Soc. Dalton Trans.*, 655–659.
[6] D.W. Cooke (1966). *Stereochemistry of Cobalt(II) Complexes*, **5**, 1114–1145.
[7] J.I. Legg and D.W. Cooke (1966). *Inorg. Chem.*, **5**, 594.
[8] I.V. Kuzmenko, T.N. Polynova, M.A. Porai-Koshits and A.L. Poznya (1992). *Koord. Kim.*, **18**, 620.
[9] A.S. Antsyshkina, G.G. Sadikov, V.S. Sergienk and A.L. Pozynka (1997). *Zh. Neorg. Khim.*, **42**, 1137.
[10] Ya. M. Nesterova, T.N. Polynova, M.A. Porai-Koshits, F.G. Kramarenko and N.M. Muratova (1979). *Zh. Strukt. Khim.*, **20**, 960.
[11] R.H. Blessing (1976). *Acta. Cryst.*, Sect. A, 33.
[12] G.M. Sheldrick (1997). *SHELXL-97*. University of Gottingen.
[13] L.J. Barbour (1999). *X-SEED Crystallographic Interface*.
[14] M. Johnson, J.C. Taylor and G.W. Cox (1980). *J. Applied Crystallogr.*, **13**, 188.