X-ray powder diffraction analysis of a silver(I) cyclamate complex

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X-ray powder diffraction data collected for the complex silver(I) cyclamate [$Ag(C_6H_{12}NO_3S)$] are reported. This material was obtained from a stoichiometric mixture of sodium cyclamate and $AgNO_3$. The analysis of the data using the Le Bail method showed that the complex has monoclinic symmetry (space group $C2/c$). The unit cell parameters are $a=31.85852(16)$ Å, $b=6.25257(6)$ Å, $c=8.46165(7)$ Å, and $\beta=95.7651(5)°$. © *2007 International Centre for Diffraction Data.*
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Key words: silver(I), cyclamate, X-ray powder diffraction, Le Bail method

I. INTRODUCTION

Silver and several silver compounds have long been used as antimicrobial agents (Klasen, 2000a, b; De Gracia, 2001; Modak *et al.*, 1983; Nomiya *et al.*, 1995, 1997; Nomiya and Yokoyama, 2002). Particularly, silver(I)-sulfadiazine has been used clinically as an antimicrobial and antifungical agent. It is an insoluble polymeric compound that releases Ag(I) ions slowly, and is applied topically as a cream to prevent bacterial infections in cases of severe burns.

Sodium cyclamate (sodium cyclohexane-sulfamate, $NaC_6H_{12}NO_3S$, see Figure 1) is a compound used as a commercial sweetener. In general, sweeteners have functional groups like carbonyl, carboxylate, amino, and sulfamate, which allow them to be used as ligands in coordination and bioinorganic chemistry. Cyclamate complexes, in general, exhibit low toxicity in humans and could be the basis of pharmaceutical products.

Considering that silver(I) compounds have antibacterial properties and that sodium cyclamate has low toxicity and low manufacture costs, a silver(I)-cyclamate complex was obtained in our laboratories. In fact, the compound reported in this paper showed a potent antimicobacterial activity against species of mycobacterium, including *mycobacterium tuberculosis*, which is responsible for tuberculosis infections. The other species tested were *mycobacterium avium*, *mycobacterium intracellulare*, *mycobacterium malmoense*, and *mycobacterium kansasii* (data not reported).

The aim of our work is to characterize the silver(I)-cyclamate complex using a collection of techniques including X-ray powder diffraction. In this contribution, the X-ray powder diffraction data for silver(I) cyclamate, $Ag(C_6H_{12}NO_3S)$, are reported.

II. EXPERIMENTAL

Sodium cyclamate (99.0% of purity) was purchased from Nutrasweet Kelco Company. Silver(I) nitrate is an Acros Organics Company product, of 99.8% purity. The compounds were used without further purification.

To synthesize the $Ag(C_6H_{12}NO_3S)$ complex, an aqueous solution of $AgNO_3$ (0.340 g, 2.0 mmol) was added under stirring to a solution containing 0.402 g (2.0 mmol) of sodium cyclamate. White crystalline powders of the complex were obtained. The compound was washed with 200 mL of water and dried over P_4O_{10} under vacuum.

Elemental analysis of carbon, hydrogen, nitrogen, and sulfur was performed using a CHNS-O EA1110 Analyzer, CE Instruments, and high purity cysteine was used as a reference substance. The silver content was determined by atomic absorption spectroscopy using an A Analyst 300 Perkin Elmer spectrometer. The infrared spectrum was recorded on a Spectrum 2000 FT-IR Perkin Elmer spectrophotometer from KBr pellets. Measured concentrations (wt.%) for $C_6H_{12}AgO_3NS$ were determined to be C, 25.5; H, 4.35; N, 5.04; S, 11.2; and Ag, 38.8%, while the calculated concentrations are C, 25.2; H, 4.23; N, 4.89; S, 11.2; and Ag, 37.7%.

III. INSTRUMENTATION

X-ray diffraction data were obtained using synchrotron radiation in the D10B-XPD line of the Laboratorio Nacional de Luz Sincrotron (LNLS) in Brazil. The experimental setup consisted of a Si (111) double-crystal monochromator with the first crystal refrigerated and the second sagitally curved. A scintillation detector was used. The monochromator was adjusted to select the energy $E=8.4995$ keV ($\lambda=1.45864$ Å), that is the energy of maximum intensity at the LNLS in Brazil. $\theta-2\theta$ geometry was used; a Y_2O_3 sample was used as reference material to check for the wavelength and instrumental broadening. The sample was deposited in a

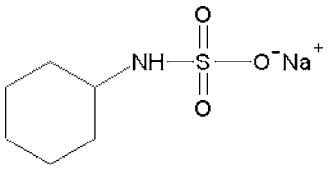

Figure 1. Schematic representation of sodium cyclamate.

TABLE I. Best solutions obtained by the program Chekcell after analysis of the results obtained by Crysfire.

	Space groups	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
1	$Cc, Ca, C2/c$	31.858	6.251	8.459	90	95.75	90
2	$Cc, Ca, C2/c$	31.874	6.253	8.462	90	95.75	90

flat sample holder of 10×12 mm^2. Data were collected from 9 to 50 °2θ, with step scan of 0.005 °2θ. The software XFit (Coelho and Cheary, 1997) was used to fit 46 peaks that were used for the indexing with the Crysfire suite (Shirley, 2002). The GSAS suite program (Larson and von Dreele, 2001) was used for the Le Bail fit. The Thompson-Cox-Hastings pseudo-Voigt function was used as the profile function. During the refinements, only the profile parameters that vary with sec θ and tg θ were refined.

IV. RESULTS AND DISCUSSION

According to the elemental analysis for C, H, N, and S, the formula of the complex is $[Ag(C_6H_{12}NO_3S)]$. The main IR features of the cyclamate ligand are 3276 cm^{-1} (s, ν N–H), 2977–2854 cm^{-1} (s, ν C–H of ring and aliphatic ring), 1488 cm^{-1} (m, δ C–H of aliphatic ring), 1246 cm^{-1} (m, δ C–N), 1213 cm^{-1} (w, $\delta_{ass.}$ SO_2 group), and 1054 cm^{-1} (w, $\delta_{sym.}$ SO_2 group) (Silverstein *et al.*, 1991). The comparison of the IR spectrum of the silver-complex with that of the sodium cyclamate indicates that the ligand is coordinated to Ag(I) through the nitrogen of the secondary amine and the oxygen of the sulfamate group.

The analysis of the diffraction data with Crysfire and Chekcell resulted in two solutions, each one with three possible space groups (Table I). All solutions were used for the Le Bail fit and the agreement factors for all six fits are in Table II. Lower χ^2 values were obtained for the first solution with the space group $C2/c$, and the unit cell parameters for this case are a=31.851 95(19) Å, b=6.250 87(6) Å, c =8.459 70(6) Å, and β=95.765(0)°. The relative intensities for the best fit are in Table III. The powder diffraction data, after the indexing, are shown in Table III. The results of the profile fit are shown in Figure 2.

Density measurements (pycnometric determination under helium, after a careful evacuation) were used to determine an experimental density of 2.375 g/cm^3. This experi-

TABLE II. Agreement factors after Le Bail fit for each solution described in Table I and unit cell parameters for the best Le Bail fit.

From solution no.		Rwp	χ^2
1	Ca	9.45	2.056
	Cc	9.46	2.059
	$C2/c$[a]	9.30	1.191
2	Ca	9.80	2.209
	Cc	9.66	2.152
	$C2/c$	9.44	2.050

[a]Best fit: a=31.85195(15) Å, b=6.25087(6) Å, c=8.45970(6) Å, β =95.765°, V=1675.828(20) Å^3.

TABLE III. Powder X-ray diffraction data for the Ag(I)-cyclamate complex.

h	k	l	d	I	h	k	l	d	I
4	0	0	7.923	999	2	0	−4	2.114	0
1	1	0	6.133	3	0	0	4	2.104	13
3	1	0	5.379	11	2	2	−3	2.090	24
6	0	0	5.282	80	0	2	3	2.088	4
1	1	−1	5.003	3	4	0	−4	2.086	2
1	1	1	4.911	20	14	0	−2	2.083	25
3	1	−1	4.642	38	13	1	−2	2.082	48
5	1	0	4.450	36	1	3	0	2.079	1
3	1	1	4.431	73	8	2	2	2.065	25
0	0	2	4.208	6	2	0	4	2.059	16
2	0	−2	4.173	88	4	2	−3	2.057	0
5	1	−1	4.054	5	2	2	3	2.050	7
2	0	2	3.970	141	3	3	0	2.044	6
8	0	0	3.961	347	10	2	−2	2.027	5
4	0	−2	3.882	36	6	0	−4	2.026	1
5	1	1	3.824	0	1	3	−1	2.022	9
7	1	0	3.667	134	12	2	0	2.017	24
4	0	2	3.571	24	1	3	1	2.015	7
1	1	−2	3.502	10	11	1	−3	2.007	21
7	1	−1	3.466	31	1	1	−4	2.002	36
6	0	−2	3.465	168	15	1	0	2.001	2
1	1	2	3.439	122	12	2	−1	1.997	41
3	1	−2	3.400	0	3	3	−1	1.995	34
7	1	1	3.266	0	3	1	−4	1.995	16
3	1	2	3.235	163	6	2	−3	1.993	4
5	1	−2	3.171	31	15	1	−1	1.990	12
10	0	0	3.169	252	9	1	3	1.986	15
6	0	2	3.141	37	4	0	4	1.985	2
0	2	0	3.125	22	4	2	3	1.983	1
9	1	0	3.068	218	16	0	0	1.981	7
2	2	0	3.066	28	5	3	0	1.979	19
8	0	−2	3.041	131	1	1	4	1.979	11
9	1	−1	2.967	12	3	3	1	1.978	4
5	1	2	2.955	107	5	1	−4	1.956	48
0	2	1	2.930	29	8	0	−4	1.941	7
4	2	0	2.907	18	5	3	−1	1.940	4
2	2	−1	2.899	5	12	2	1	1.928	0
7	1	−2	2.883	83	3	1	4	1.926	10
2	2	1	2.863	35	13	1	2	1.925	85
9	1	1	2.804	40	14	0	2	1.915	8
4	2	−1	2.780	0	5	3	1	1.913	4
8	0	2	2.750	47	10	2	2	1.912	10
4	2	1	2.717	43	15	1	1	1.907	25
6	2	0	2.690	31	8	2	−3	1.907	25
10	0	−2	2.663	73	6	2	3	1.894	6
7	1	2	2.659	41	7	3	0	1.893	7
12	0	0	2.641	335	7	1	−4	1.893	9
11	1	0	2.616	177	6	0	4	1.891	13
6	2	−1	2.601	7	15	1	−2	1.878	32
9	1	−2	2.589	80	1	3	−2	1.869	2
1	1	−3	2.570	1	16	0	−2	1.866	20

TABLE III. (*Continued.*)

h	*k*	*l*	*d*	*I*	*h*	*k*	*l*	*d*	*I*
11	1	−1	2.566	11	1	3	2	1.859	2
3	1	−3	2.541	0	3	3	−2	1.853	4
1	1	3	2.533	3	5	1	4	1.852	2
6	2	1	2.525	41	13	1	−3	1.852	1
0	2	2	2.509	1	10	0	−4	1.840	9
2	2	−2	2.501	12	14	2	0	1.833	39
2	2	2	2.456	2	11	1	3	1.832	4
8	2	0	2.454	0	7	3	1	1.830	0
5	1	−3	2.453	1	3	3	2	1.825	3
3	1	3	2.437	4	14	2	−1	1.822	16
11	1	1	2.436	11	5	3	−2	1.813	1
4	2	−2	2.434	9	9	1	−4	1.811	0
10	0	2	2.418	51	10	2	−3	1.807	2
8	2	−1	2.396	35	9	3	0	1.793	4
9	1	2	2.382	0	8	2	3	1.793	0
4	2	2	2.352	10	17	1	0	1.786	25
12	0	−2	2.345	4	8	0	4	1.785	1
7	1	−3	2.321	32	17	1	−1	1.783	6
6	2	−2	2.321	38	9	3	−1	1.772	2
11	1	−2	2.319	82	12	2	2	1.767	11
8	2	1	2.317	15	7	1	4	1.764	10
5	1	3	2.301	4	14	2	1	1.762	7
13	1	0	2.271	74	18	0	0	1.761	13
14	0	0	2.264	39	7	3	−2	1.754	2
13	1	−1	2.246	2	2	2	−4	1.751	1
10	2	0	2.225	20	0	2	4	1.745	17
6	2	2	2.216	17	15	1	2	1.744	93
10	2	−1	2.190	31	9	3	1	1.736	5
8	2	−2	2.180	46	4	2	−4	1.735	2
9	1	−3	2.167	28	12	0	−4	1.733	4
7	1	3	2.145	3	14	2	−2	1.733	9
13	1	1	2.143	39	16	0	2	1.727	13
12	0	2	2.142	50	2	2	4	1.719	19
11	1	2	2.136	20	11	1	−4	1.718	20

mental value, combined with the molar mass of the complex, allowed for the calculation of the number of formula weight contained in a cell, equal to 8 ($Z=8$).

V. CONCLUSION

A new silver(I)-cyclamate complex that presents a potent antimicobacterial activity against species of mycobacterium, including *mycobacterium tuberculosis*, has been prepared and characterized using X-ray powder diffraction. The formula of the complex, determined by elemental analysis, is $Ag(C_6H_{12}NO_3S)$. At room temperature the silver(I)-cyclamate complex has monoclinic symmetry with unit cell parameters $a=31.858\,52(16)$ Å, $b=6.2526(6)$ Å, $c=8.461\,65(7)$ Å, and $\beta=95.7651(5)°$, with three space groups being possible ($C2/c$, Cc, Ca). Crystal structure determination is necessary for the definition of the space group.

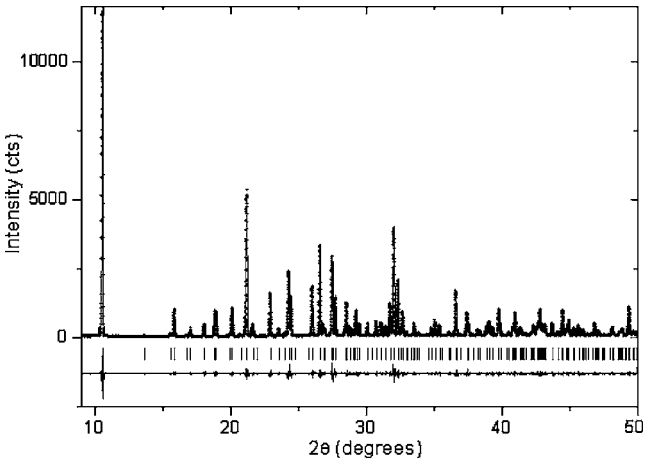

Figure 2. Observed (dots), fitted (continuous line), and difference (bottom line) diffractograms for silver(I)-cyclamate. The small vertical lines above the difference plot are the Bragg peak positions.

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