Tentative Partial Oxidation of the Nickel(II) Potassium-dithiooxalato Complex: Existence of an Iodine Adduct $K_2Ni(S_2C_2O_2)_2I$ in Solution and Crystal Structure of a New Polymorphic Form of $K_2Ni(S_2C_2O_2)_2$ ('Black' Form)

A. GLEIZES*, F. CLERY, M. F. BRUNIQUEL and P. CASSOUX

Laboratoire de Chimie de Coordination C.N.R.S., Université Paul Sabatier, 205, rte de Narbonne, 31400 Toulouse, France

Received January 27, 1979

Tentative partial oxidation of 'red' nickel(II) potassium-dithiooxalate $K_2Ni(S_2C_2O_2)_2$ by iodine results in a $K_2Ni(S_2C_2O_2)_2I$ adduct. This adduct was identified in solution but could not be isolated in the solid state. Operating with $K_2Cr_2O_7$ surprisingly leads to a polymorphic 'black' form of $K_2Ni(S_2C_2-O_2)_2$ which is also obtained as by-product of the rapid decomposition of the iodine adduct. The X-ray structure of the new 'black' form has been solved ($P2_1/n$; $Z = 2$; $a = 11.0369(10)$ Å, $b = 4.1911(3)$ Å, $c = 12.7221(17)$ Å, $\beta = 111.784(9)°$). Full-matrix least-squares refinement of 70 variables gave a final value of the conventional R index (on F) of 0.022 for 1420 reflections having $F_o^2 > 3\sigma$ (F_o^2). Planar $Ni(S_2C_2O_2)_2$ units stack along the b direction (Ni–Ni = 4.19 Å) which is not the case in the 'red' form. Crystallographic relationship between both 'red' and 'black' species is discussed.

Introduction

The chemical and physical properties of partially oxidized systems have been the subject of extensive recent work [1]. Partial oxidation of bis(oxalato) platinate complexes leading to highly 1-D conducting species has been demonstrated [2] and it was tempting to extend the investigations to bis(dithiooxalato) metal complexes. However, preliminary studies have failed in the case of Pt(II) complexes [3].

On the other hand, the use of iodine as an acceptor in stacked square planar metal complexes such as $M(dpg)_2I$ (dpg = diphenylglyoximate, M = Ni, Pd) has provided new examples of 1-D mixed valence compounds with high conductivity [4, 5].

Nickel(II) potassium-dithio-oxalate $K_2Ni(Dto)_2$ was first prepared and investigated by Robinson and

Jones in 1912 [6]: this salt crystallises from hot water in dark red octahedra and below room temperature needles separate. Both forms have the same composition and this was found to be a case of dimorphism by these authors. However, in 1935, Cox and col. [7] investigating the X-ray crystal structure of nickel, palladium and platinum dithio-oxalates established the planar configuration of $M(Dto)_2^{2-}$ and rejected the hypothesis of dimorphism for the nickel compound. They found the "large irridescent bipyramids" to be monoclinic (space group: $A2/a$) with $a = 10.99$ Å, $b = 7.80$ Å, $c = 22.23$ Å and $\beta = 144.°01'$. Incidentally, Coucouvanis and col. [8] have reinvestigated the crystal structure of $K_2Ni-(Dto)_2$ and refined the parameters reported by Cox.

We report here the results of tentative partial oxidation of the 'red' Ni(II) potassium-dithioxalato complex, $K_2Ni(Dto)_2$: (i) the reaction with iodine leads to a $K_2Ni(Dto)_2I$ adduct which proved stable in solution and (ii) the oxidation with $K_2Cr_2O_7$ leads to a new 'black' crystal form of $K_2Ni(Dto)_2$, the structure of which being strikingly different from the one reported for the 'red' form.

Experimental

Materials

$K_2(S_2C_2O_2)_2$ was purchased from Eastman Kodak. The 'red' $K_2Ni(S_2C_2O_2)_2$ compound was prepared according to the literature [6, 7].

Physical Measurements

Visible and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Electronic microprobe analyses were performed with a Cameca Model MS 46.

A Guinier- de Wolf camera utilizing monochromatized copper radiation was used to obtain the X-ray powder patterns of the complexes. The precession method with MoKα radiation was used for the single crystal examination.

TABLE I. Structural Data.

1) *Physical and crystallographic data:*

Formula: $K_2Ni(S_2O_2C_2)_2$

Crystal system: monoclinic

Space group: $P2_1/n$

$a = 11.0369(10)$ A

$b = 4.1911(3)$ A

$c = 12.7221(17)$ A

$\beta = 111.784(9)°$

Molecular weight: 377.21 uma

$\rho_{meas.} = 2.29(1)$ g cm^{-3}

$\rho_X = 2.292$ g cm^{-3}

$V = 546.5$ A^3

$Z = 2$

Morphology: oblical prism $0.01 \times 0.006 \times 0.025$ cm

Absorption factor: $\mu = 32.65$ cm^{-1}

2) *Data collection*

Temperature: 20 °C

Radiation: molybdenum $\lambda(K\bar{\alpha}) = 0.71069$ A

Monochromatization: oriented graphite crystal

Crystal–detector distance: 207 mm

Detector window: height[a] = 4mm, width[a] = $(1.55 + 3.30 \tan\theta)$ mm

Take-off angle[a]: 2.4°

Scan mode: $\theta - 1.333\theta$

Maximum Bragg angle: 31°

Scan angle: $\Delta\theta = \Delta\theta_0 + B\tan\theta$; $\Delta\theta_0$[a] = 0.95; B[a] = 0.35

Values determining the scan speed: SIGPRE[a] = 0.50   SIGMA[a] = 0.018

VPRE[a] = 10 °/mn   TMAX[a] = 50 s

Control:	Intensity	Orientation
Reflexions:	4 0 $\bar{8}$, 1 $\bar{2}$ $\bar{1}$, 0 1 $\bar{3}$	2 $\bar{2}$ $\bar{4}$, 3 $\bar{2}$ $\bar{7}$, 0 1 3
Periodicity:	3600 s	100 reflexions

3) *Conditions for refinement:*

Reflexions for the refinement of the cell dimensions: 25

Recorded reflexions: 2782

Independent reflexions: 2403

Utilized reflexions: 1420 ($F_o^2 > 3$ $\sigma(F_o^2)$ Refined parameters: 70

Reliability factors: $R = \Sigma||F_o| - |F_c||/\Sigma k|F_o| = 0.022$

$R_w = [\Sigma w(k|F_o| - |F_c|)^2/\Sigma wk^2 F_o^2]^{1/2} = 0.026$

$w = 4 F_o^2/\sigma^2(F_o^2)$

[a]These values are determined experimentally; they were defined in a previous paper: A. Mosset, J. J. Bonnet and J. Galy, *Acta Cryst., B33*, 2639 (1977).

X-ray Diffraction Measurements. Collection and Reduction of Data

A single crystal of 'black' $K_2Ni(Dto)_2$ was mounted on a CAD-4 Enraf-Nonius PDP8/M computer monitored diffractometer, using Mo Kα radiation monochromatized by an oriented graphite crystal. The unit-cell constants were refined by optimizing the setting angles of 25 reflections. Physical and crystallographic data along with data collection conditions are listed in Table I. The measured intensities were corrected for Lorentz and polarisation factors, and assigned standard deviations according to the classical formula using a p coefficient selected as 0.03. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques. The quantity minimized is $\Sigma w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factor amplitudes put on the same scale. The weight w and the reliability factors R and R_w are defined in part 3 of Table I. For all atoms scattering factors along with the appropriate anomalous dispersion terms were drawn from ref. [9].

Results and Discussion

The $K_2Ni(Dto)_2I$ Adduct

The addition of a solution of iodine in methanol to $K_2Ni(Dto)_2$ in water is followed by rapid decom-
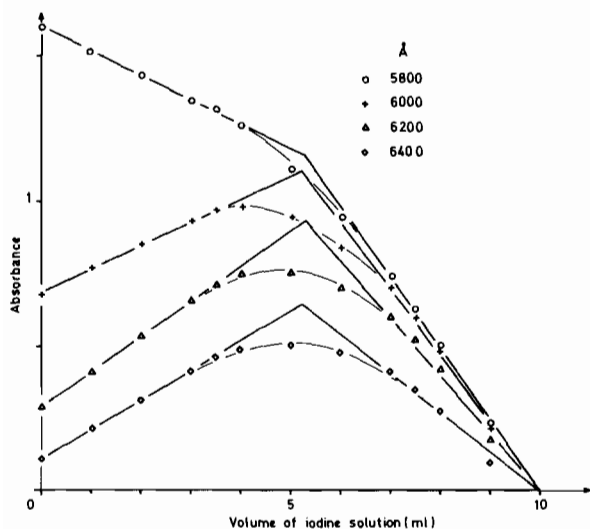
Fig. 1. Absorbance of mixtures of equimolecular (10^{-3} M) solutions of $K_2Ni(Dto)_2$ and iodine in acetone (total volume 10 ml) at selected wavelengths.

Fig. 2. Absorbance of mixtures of acetone solutions of K_2-$Ni(Dto)_2$ and iodine. The (Ni) concentration (2×10^{-4} M) has been held constant while the (I)/(Ni) ratios were varied.

position of the complex. By contrast, the addition of iodine in acetone or acetonitrile to $K_2Ni(Dto)_2$ in the same solvents is accompanied by a change in colour of the solutions from purple to blue. With increasing iodine concentration changes occur in the spectra of these solutions (*cf.* Fig. 2): (i) the absorption band at 5050 and 5650 Å (lit. [7]: 5025 and 5618 Å, respectively) shift to lower energy, and (ii) a new band is observed at ~6050 Å. The kinetics of the reaction is slow and the pattern of the spectra stabilizes after 48 hours at room temperature. These facts indicate the formation of a complex between $K_2Ni(Dto)_2$ and iodine.

The stoichiometry of this adduct was determined by use of the continuous variation method [10]: the absorbance at selected wavelengths was measured for a series of mixtures of equimolecular solutions (10^{-3} M) of $K_2Ni(Dto)_2$ and iodine in acetone (or aceto-nitrile). Figure 1 clearly shows that the stoichiometry of the adduct is 1:1. However the smooth curve in the region of the maximum is characteristic of an equilibrium reaction and indicates that the adduct is not very stable in solution.

As $K_2Ni(Dto)_2$ and $K_2Ni(Dto)_2I$, which seem to exist in equilibrium, exhibit overlapping absorption bands, the method of the 'isosbestic' point was used to confirm the existence of the iodine adduct [11]: by mixing solutions of $K_2Ni(Dto)_2$ and iodine, the (Ni) concentration being held constant while the (I)/(Ni) ratios being varied, the absorption curves of these mixtures intersect at a fixed wavelength 5575 Å (Fig. 2). The existence of this isosbestic point shows that there are only two species present in solution, *i.e.*, $K_2Ni(Dto)_2$ and $K_2Ni(Dto)_2I$, with equal extinction coefficients (2250) at this wavelength.
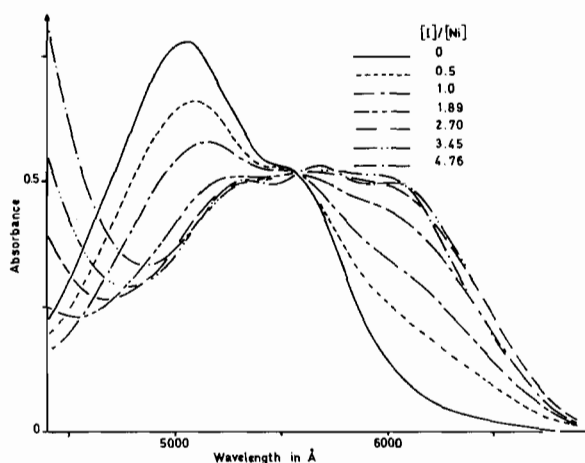
As noted above, $K_2Ni(Dto)_2I$ is not very stable in solution, nor it is in the solid state; the crystals obtained by evaporation of solutions in acetone or acetonitrile of $K_2Ni(Dto)_2$ and iodine were charac-terized by C and Ni analyses corresponding to the $K_2Ni(S_2C_2O_2)_2$ formula. Any attempt to isolate the $K_2Ni(Dto)_2I$ adduct, by varying the solvent, the excess of iodine, the solvent evaporation rate and the temperature failed. In some cases, crystals obtained by rapid evaporation of the solvent at low tempera-ture (~ -5 °C) and under vacuum, were rapidly dissolved again in acetone and the electronic spectra indicated that the $K_2Ni(Dto)_2I$ adduct was still present in these solutions. Apparently during the crystallisation process (or after), iodine is released and this explains why the adduct could not be isolated.

However, the black colour of the thus obtained crystals was strikingly different from the red colour of the starting $K_2Ni(Dto)_2$ material. As a matter of fact, the X-ray powder patterns of these crystals show that they are a mixture of the red initial K_2-$Ni(Dto)_2$ and of a new 'black' crystal form which has been alternatively obtained while trying to achieve partial oxidation with $K_2Cr_2O_7$ instead of iodine.

The $K_2Ni(Dto)_2$ 'Black' Form

When red crystals of $K_2Ni(Dto)_2$ are heated in a dilute solution of potassium dichromate according to the oxidative method of Krogmann and col. [12], a blend of red and black crystals is obtained on evaporating the solution. The red crystals were rapidly identified as the initial compound. The black crystals appeared as glittering prismatic crystals. They were submitted to electronic microprobe and to X-ray analysis. Microprobe analysis revealed them to contain nickel, potassium and sulfur elements. From X-ray precession photographs they could be

TABLE II. Positional and thermal parameters for the atoms of black $K_2Ni(S_2C_2O_2)_2$.[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0	0	3.04(3)	34.35(20)	3.15(2)	0.39(6)	0.84(2)	−0.73(5)
K	0.46786(4)	−0.29556(11)	−0.16012(3)	5.17(4)	36.45(25)	4.03(3)	0.90(8)	1.34(3)	0.53(7)
S(1)	0.01825(4)	−0.28695(13)	−0.13614(4)	3.78(4)	47.1(3)	3.67(3)	−1.02(9)	0.94(3)	−3.09(8)
S(2)	0.21156(4)	0.01591(13)	0.08982(4)	3.51(4)	49.6(3)	3.83(3)	0.47(9)	0.79(3)	−3.75(8)
O(1)	0.22829(14)	−0.4945(4)	−0.16098(13)	5.46(13)	71.0(12)	6.30(12)	−4.7(3)	3.15(10)	−9.3(3)
O(2)	0.39497(12)	−0.2149(3)	0.02898(11)	3.47(10)	43.6(8)	4.66(9)	1.56(26)	1.09(8)	−1.23(24)
C(1)	0.18212(17)	−0.3408(5)	−0.10240(15)	4.49(15)	37.2(12)	3.90(12)	−2.2(3)	1.86(11)	−1.7(3)
C(2)	0.27647(16)	−0.1859(4)	0.00715(14)	3.78(14)	28.0(9)	3.63(11)	0.5(3)	1.10(10)	0.97(26)

[a]Estimated standard deviations in the least significant figure(s) are given in parentheses. The form of the anisotropic thermal ellipsoid is $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. The quantities given in the table are the thermal coefficients $\times 10^3$.

TABLE III. Root-mean-square Amplitudes of Vibration (A).

Atom	Minimum	Intermediate	Maximum
Ni	0.1266(5)	0.1525(5)	0.1771(5)
K	0.1604(5)	0.178(3)	0.182(3)
S(1)	0.1378(6)	0.1616(7)	0.2128(7)
S(2)	0.1349(6)	0.1579(7)	0.2234(7)
O(1)	0.153(2)	0.171(2)	0.282(2)
O(2)	0.134(2)	0.180(2)	0.206(2)
C(1)	0.146(3)	0.159(3)	0.191(3)
C(2)	0.140(3)	0.155(3)	0.169(3)

assigned monoclinic symmetry, space group $P2_1/n$, and cell constants $a = 11.05$ Å, $b = 4.19$ Å, $c = 12.74$ Å and $\beta = 111.8°$. These are not the crystallographic characteristics of red crystals of $K_2Ni(Dto)_2$. However the two kinds of crystals have cell volumes in the ratio 1:2; moreover a measure of the density of black crystals by flotation in iodomethane ($d_4^{20} = 2.279$) against temperature led to $\rho = 2.29$ g/cm^3 which is very close to the density of the red crystals, $\rho = 2.23$ g/cm^3. These common features joined to the qualitative microprobe analysis results led to assume that both black and red crystals have the same chemical formula. This would mean that partial oxidation of red crystals did not occur during the experiment related above, at least at an appreciable extent. Indeed this was later confirmed by the X-ray structure solution which will be described now.

Crystal Structure of 'Black' $K_2Ni(Dto)_2$

Structure solution and identification

One must keep in mind that when starting this structure determination we did not know the right stoichiometry of the compound.

The display of the strongest peaks in the Patterson map suggested the presence in the cell of two NiS_4 groups with the Ni atoms in a special position (0, 0, 0; ½, ½, ½) and the four S atoms located at the corners of a planar square around it. Initial refinement of the Ni and the S atom positions, isotropic thermal parameters and scale factor led to a R index of 0.445. A subsequent Fourier map showed two independent maxima of electron density which were attributed to K atoms. This was confirmed by two more cycles which resulted in R = 0.252. Then, on an ensuing Fourier map, maxima could be unambiguously attributed to O and C atoms completing the geometries of the dithio-oxalato groups. These atoms were introduced in the refinement. The discrepancy factors dropped to R = 0.102 and R_w = 0.132. Next, the atoms were given anisotropic thermal parameters and the reliability factors were R = 0.026 and R_w = 0.031 after two more cycles. An absorption correction was made, based on $\mu = 32.65$ cm^{-1}; the transmission factors ranged from 0.686 to 0.823. In the last cycle of refinement the reliability factors are stabilized at R = 0.022 and R_w = 0.027. Seventy parameters were refined for the 1420 observations used. The error in the observation of unit weight was 1.1 electron.

The final positional and thermal parameters are listed in Table II. Root mean-square amplitudes of vibration of the atoms are given in Table III. A listing of the observed and calculated structure amplitudes is available.

Description of the structure

A ball and spoke drawing of the structure in projection onto the (010) plane and a stereoview of the structure down the b axis are given in Fig. 3a and 3b. Selected distances and angles appear in Table IV. This structure consists of columns of stacked planar $Ni(Dto)_2$ units and of linear chains of K atoms. Both columns and chains run parallel to the b axis with Ni–Ni and K–K intervals equal to the b parameter, i.e. 4.1911(4) Å. The $Ni(Dto)_2$ units are not perpendicular to the piling direction but make an angle of 124° with it.
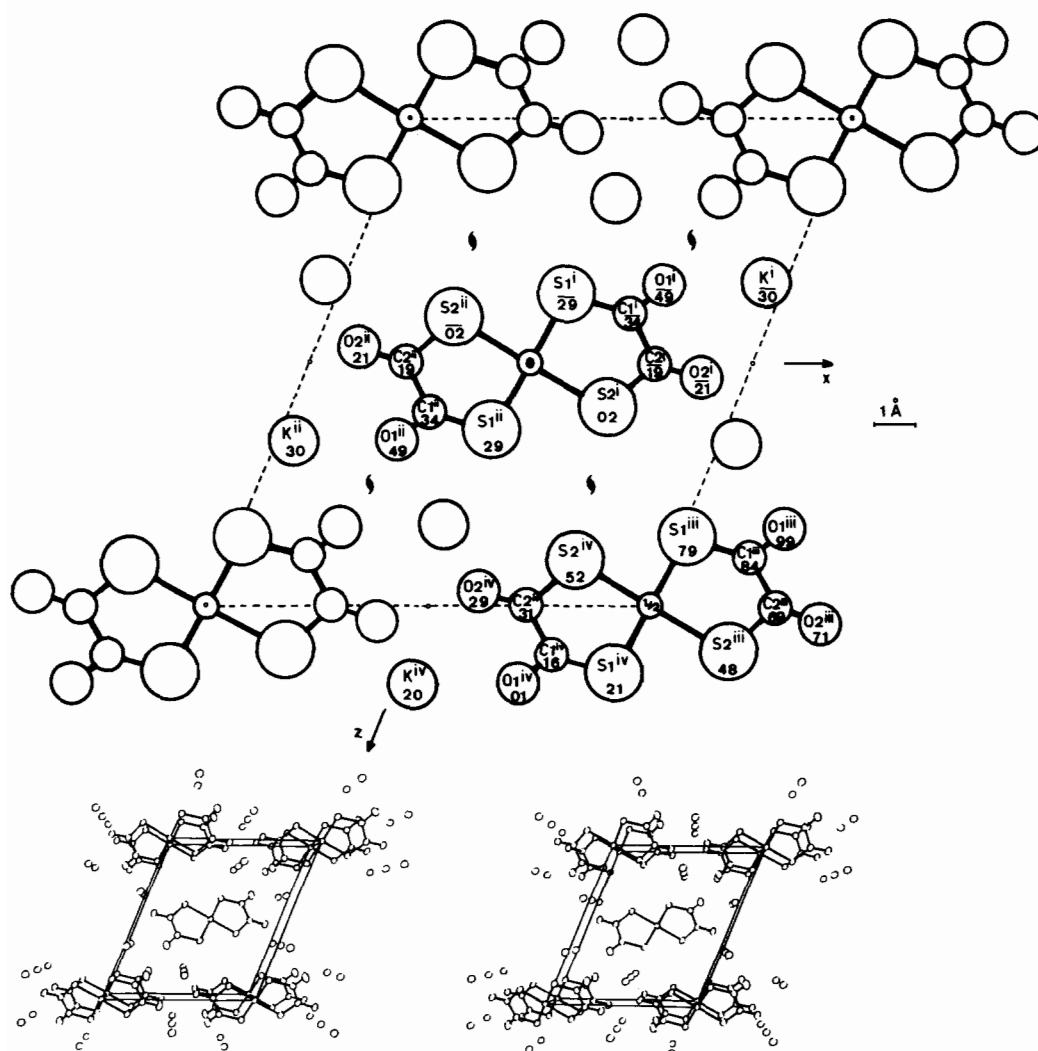
Fig. 3. (a) Ball and spoke drawing of the 'black' $K_2Ni(Dto)_2$ in projection onto the (010) plane. (b) Stereoscopic view down the *b* axis of the unit cell of 'black' $K_2Ni(Dto)_2$ showing the stacking of $Ni(Dto)_2$ groups and K atoms.

TABLE IV. Selected Interatomic Distances (Å) and Bond Angles (deg) in Black $K_2Ni(S_2C_2O_2)_2$.

TABLE IV. *(Continued)*

S(2)–C(2)	: 1.701(2)	S(1)–C(1)–O(1)	: 123.6(2)
C(1)–C(2)	: 1.540(3)	O(1)–C(1)–C(2)	: 118.4(2)
C(1)–O(1)	: 1.230(2)	S(2)–C(2)–C(1)	: 118.1(1)
C(2)–O(2)	: 1.238(2)	S(2)–C(2)–O(2)	: 124.2(1)
S(1)–O(1)	: 2.603(2)	O(2)–C(2)–C(1)	: 117.7(2)
S(2)–O(2)	: 2.607(1)	Ni–S(1)–C(1)	: 105.9(7)
O(1)–O(2)	: 2.702(2)	Ni–S(2)–C(2)	: 105.9(6)

Code of equivalent positions used in this table:

i:	x, y, z	v:	$1 - x, -1 - y, \bar{z}$
ii:	$\bar{x}, \bar{y}, \bar{z}$	vi:	$1 - x, \bar{y}, \bar{z}$
iii:	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	vii:	$\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$
iv:	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	viii:	x, 1 + y, z
		ix:	$\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$

Around Nickel:

Ni–S(1)	: 2.1785(5)	S(1)[i]–Ni–S(2)[i]	: 92.09(2)
Ni–S(2)	: 2.1867(4)	S(1)[i]–Ni–S(2)[ii]	: 87.91(2)
Ni[i]–Ni[viii]	: 4.1911(4)		

Around Potassium:

K–O(2)[v]	: 2.722(2)	K–S(1)[ix]	: 3.3583(8)
K–O(1)[i]	: 2.769(2)	K–S(1)[vii]	: 3.4030(7)
K–O(2)[vi]	: 2.789(2)	K–S(2)[vi]	: 3.5134(7)
K–O(1)[vii]	: 2.793(2)	K[i]–K[viii]	: 4.1911(4)
K–O(2)[i]	: 2.826(2)	K[i]–K[v]	: 4.230(1)
		K[i]–K[vii]	: 4.958(1)

Dithioxalato group:

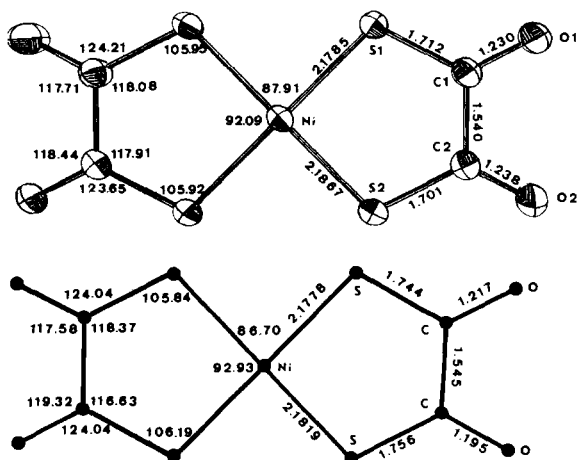|			
S(1)–C(1)	: 1.712(2)	S(1)–C(1)–C(2)	: 117.9(1)

Fig. 4. (a) A drawing of the Ni(Dto)$_2^{2-}$ anion in the 'black' form: the atoms are drawn at their 50% probability ellipsoids. (b) A sketch of the same anion in the 'red' form.
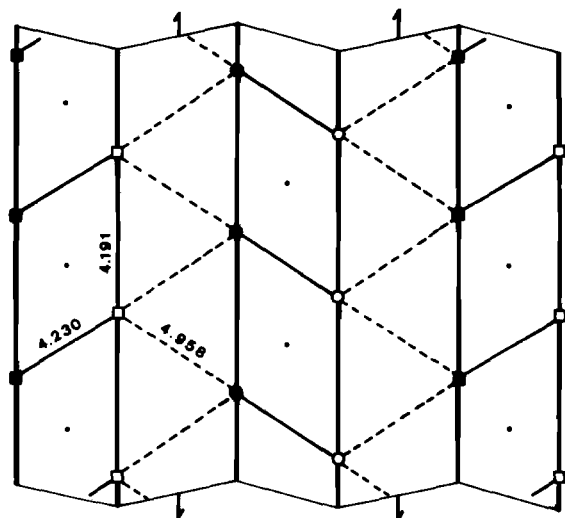

Fig. 6. Projection of the 'black' structure on the (010) plane showing the sequence of K atom layers and Ni(Dto)$_2$ group layers. A Ni(Dto)$_2$ group is represented by its nickel atom (○: y = 0; ●: y = ½) surrounded by the parallelogram built on the oxygen atom positions. K–O bonds are shown by weak lines. For the sake of clarity K–S bonds are not drawn.

Fig. 5. A drawing of a K atoms layer in the 'black' form (■: y = 0.28; □: y = 0̄.2̄8̄; ●: y = 0.22; ○: y = 0̄.2̄2̄).

The geometry of the anion Ni(Dto)$_2^{2-}$ is shown in Fig. 4a with selected bond lengths and angles; the geometry of the same anion in the red form is sketched in Fig. 4b, for the sake of comparison, with reported values drawn from Coucouvanis *et al.*'s structural work [8]. In the black form the nickel atom lies on a center of symmetry; it is coordinated to two thioxalato groups through the sulfur atoms located at the corners of a planar square. Ni–S distances range over two slightly different values: 2.1785(6) Å and 2.1867(4) Å. Also do the S–Ni–S angles: 92.09(2)° and 87.91(2)°. The quasi planarity
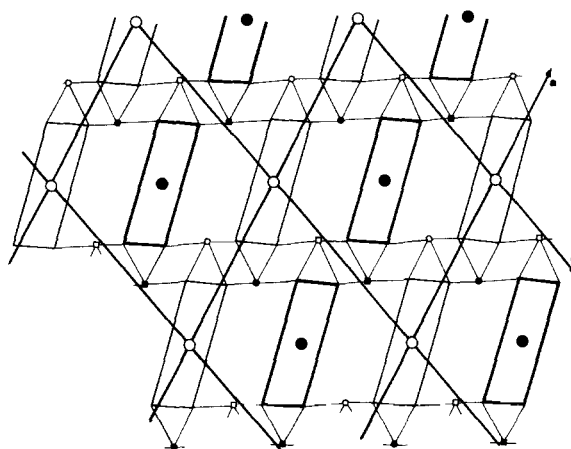
of the Ni(Dto)$_2^{2-}$ anion is attested to in that none of its constituting atoms is more than 0.06 Å out of the least squares plane which can be fitted to include them. Differences concerning the Ni(Dto)$_2^{2-}$ anion in both the red and black forms are minor: in the former, the coordination is not exactly planar but slightly tetrahedral and S–C bond lengths are larger than in the latter while C–O bonds are shorter (Fig. 4).

In the black species, potassium atoms are close to five oxygen atoms and to three sulfur atoms. K–O and K–S shortest contacts range from 2.722(1) to 2.826(1) Å and from 3.3583(8) to 3.5134(7) Å respectively. These distances compare fairly with the sum of ionic radii [13]: 2.87 Å for K–O and 3.35 Å for K–S. The coordination polyhedron around K$^+$ cannot be related to any regular shape. In the potassium network we can notice that each atom is surrounded by five other potassium atoms: two of them are on the same chain at 4.1911(4) Å; a third one at 4.230(1) Å is located on the neighbouring chain through the center of symmetry; two others are at 4.958(1) Å on the neighbouring chain through the 2$_1$ axis (Fig. 5).

As shown in Figs. 5 and 6, potassium atoms display a layered framework in which sheets of Ni(Dto)$_2$ groups are enclosed, the mean plane of which being parallel to the (10$\bar{1}$) plane. The cohesion of the structure is ensured by the K–O and K–S contacts only, for there are no van der Waals' contacts between Ni(Dto)$_2^{2-}$ anions: as a matter of fact closest interanionic O–O, O–S and S–S distances are respectively 3.230(2), 3.855(2) and 3.972(1) Å which are significantly larger than the sums of the corresponding van der Waals' radii (r$_O$ = 1.40 Å; r$_S$ = 1.85 Å [14]).
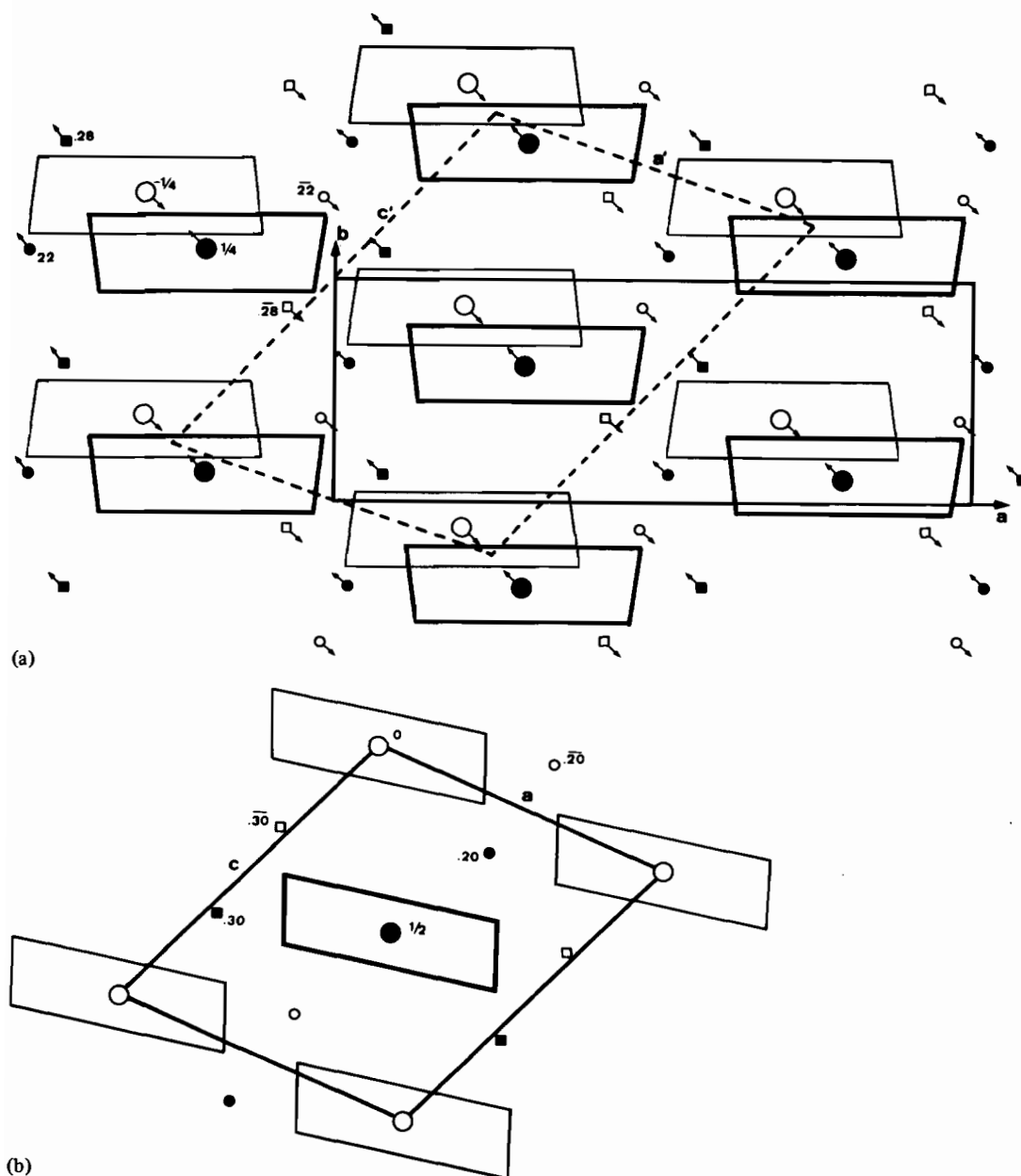
(a)

(b)

Fig. 7. Structural relationship between (a) the 'red, and (b) the 'black' form (see text).

Discussion

It is worthwhile to understand from a chemical point of view what happens when going from the red to the black crystals of $K_2Ni(Dto)_2$.

As previously reported, attempts to isolate the $K_2Ni(Dto)_2I$ adduct in the solid state yielded a black crystalline compound which exhibited the same X-ray powder pattern as the black $K_2Ni(Dto)_2$ new species obtained in the presence of $K_2Cr_2O_7$. From the X-ray structural study it is obvious that this new species is not a 'mixed valence' compound but a polymorphic

form of the red $K_2Ni(Dto)_2$. Then the role of an oxidant as I_2 or $K_2Cr_2O_7$ may be questioned. Moreover further experiments have shown that black $K_2Ni(Dto)_2$ crystals can be also obtained on evaporating solution of the red species in presence of a reductive agent.

The comparison of the structures of both red and black forms sheds some light on this matter: indeed, there is a straightforward relationship between both structures. In Fig. 7a is presented a projection of the structure of the red species onto the (001) plane along a direction perpendicular to this plane. The c

axis makes an angle of 143.92° with the *a* axis. The two structures are fundamentally different in that there is no linear stacking in the red form. In this species, Ni(Dto)$_2$ units are nearly parallel to the (001) plane; closest Ni–Ni and K–K distances are 5.843(3) and 4.344(3) Å, respectively.

The crystal structure of the red form may be derived from the black one in the following manner: let first couples of Ni(Dto)$_2$ groups and couples of K atoms in the red form be brought into coincidence as indicated by the arrows in Fig. 7a; one gets then a new monoclinic cell (dotted lines). The estimated parameters of this new cell are: $a' \cong 11.9$ Å; $c' \cong 16.2$ Å, $\beta' \cong 113°$ whilst a value close to 7.863 Å x sin(143.92) $\cong 4.6$ Å can be deduced for the new b' parameter. This new cell compares rather well with the one of black crystals (Fig. 7b): $a = 11.037$ Å; $b = 4.191$ Å; $c = 12.722$ Å; $\beta = 111.72°$. In order to get the actual 'black' structure, this first rearrangement should be completed by (i) the tilting of the Ni(Dto)$_2$ planar units with respect to the $a'c'$ plane, and (ii) the redistribution of Ni(Dto)$_2$ units over $y' = 0$ and $y' = \frac{1}{2}$ whilst K atoms are situated around planes $y' = \frac{1}{4}$ and $y' = \frac{3}{4}$. This redistribution of cell content over 4 levels allows for a reduction of the $(a'b'c')$ cell volume since in the starting cell Ni(Dto)$_2$ groups and K atoms are located around only 2 levels, $z = \frac{1}{4}$ and $z = \frac{3}{4}$. In fact the 'black' cell has the same volume per unit formula (273.3 Å^3) as the 'red' one (274.4 Å^3).

Acknowledgements

References

1 J. S. Miller and A. J. Epstein, *Progr. Inorg. Chem.*, 20 (1976).
2 F. N. Lecrone, M. J. Minot, and J. H. Perlstein, *Inorg. Nucl. Chem. Lett.*, *8*, 173 (1972); T. W. Thomas, C. Hsu, M. M. Labes, P. S. Gomm, A. E. Underhill and D. M. Watkins, *J. Chem. Soc. Dalton*, 2050 (1972).
3 Ref. 335 in [1].
4 A. Gleizes, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, *97*, 3545 (1975).
5 M. A. Cowie, A. Gleizes, G. W. Grynkewich, D. W. Kalina, M. S. Mc Clure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, *101*, 2921 (1979).
6 C. S. Robinson and H. O. Jones, *J. Chem. Soc.*, *101*, 62 (1912).
7 E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).
8 D. Coucouvanis, N. C. Baenzinger and S. M. Johnson, *J. Am. Chem. Soc.*, *95*, 3875 (1973).
9 D. T. Cromer and J. T. Waber 'International Tables for X-ray Crystallography', Vol IV, Table 2.2 A, Kynoch Press, Birmingham (1974); D. T. Cromer, *ibid.*, Table 2.3.1.
10 P. Job, *Ann. Chim.*, *9*, 113 (1928).
11 P. Souchay and J. Lefebvre, in 'Equilibres et Réactivité des Complexes en Solution', Masson, Paris (1969).
12 K. Krogmann and P. Dodel, *Chem. Ber.*, *99*, 3402 (1966).
13 R. D. Shannon and C.T. Prewit, *Acta Cryst.*, *B25*, 925 (1969).
14 L. Pauling, 'The Nature of the Chemical Bond', 3rd Edn., Cornell University Press, Ithaca, N.Y (1960).