

AD-A070 441

VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY
SYNTHESIS, ELECTRICAL CONDUCTIVITY, AND MAGNETISM OF A NEW MOLE--ETC(U)
JUN 79 J T WROBLESKI, D B BROWN
TR-16

F/G 7/3
N00014-75-C-0756
NL

UNCLASSIFIED

| OF |
AD
A070441



END
DATE
FILMED
7-79
DDC

AD A 070 441

DDC FILE COPY

LEVEL

12

OFFICE OF NAVAL RESEARCH

Contract ¹⁵ N00014-75-C-0756

Task No. NR 356-593

⁹ TECHNICAL REPORT NO. 16

⁶ Synthesis, Electrical Conductivity, and Magnetism of a New Molecular Metal,
 $K_2[Ni(1,2-dithiooxalate)_2] \cdot 1.0$

by

¹⁰ James T. Wroblewski and David B. Brown

Prepared for publication in the

Journal of the American Chemical Society

University of Vermont

Department of Chemistry

Burlington, Vermont 05405

¹¹ 11 June 1979

¹² 12p.

¹⁴ TR-16

DDC
RECEIVED
JUN 26 1979
C

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

408 892

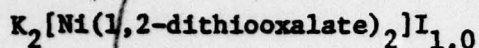
LB

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 16	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "Synthesis, Electrical Conductivity, and Magnetism of a New Molecular Metal, $K_2[Ni(1,2\text{-dithiooxalate})_2]I_{1.0}$ "		5. TYPE OF REPORT & PERIOD COVERED Technical Report
7. AUTHOR(s) James T. Wroblewski and David B. Brown		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Vermont Burlington, Vermont 05405		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0756
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE June 11, 1979
		13. NUMBER OF PAGES 7
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted for publication in the Journal of the American Chemical Society		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Molecular metal, electrical conductivity, solid-state oxidation, stacked metal complex		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Samples of $K_2[Ni(DTO)_2]I_{1.0}$ (DTO = 1,2-dithiooxalate) have been prepared by either solid-state oxidation of $K_2[Ni(DTO)_2]$ with excess I_2 at 130-140°C or electrolysis of $K_2[Ni(DTO)_2]$ in methanol solution saturated with tetraethylammonium iodide. This material exhibits metal-like electrical conductivity ($\sigma^{300K} \approx 500 \Omega^{-1} \text{ cm}^{-1}$) which, for one sample (sample A), persists to the lowest temperature at which data were obtained (20 K). Other samples of $K_2[Ni(DTO)_2]I_{1.0}$ undergo a metal-to-insulator transition at temperatures		

as high as 190 K. Variable-temperature (20-300 K) magnetic susceptibility data for sample A were obtained. The effective magnetic moment for sample A decreases from $2.4\mu_B$ at 295 K to $2.2\mu_B$ at 40 K. Below 40 K the value of μ_{eff} increases and becomes field dependent. A bonding model for this material is proposed.

Accession For	
NTIS GNA&I	☒
DDC TAB	☐
Unannounced	
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	

Synthesis, Electrical Conductivity, and Magnetism of a New Molecular Metal,



Sir:

Mixed-valence, linear-chain polymers which possess relatively high electrical conductivity have been prepared from square-planar ⁸ transition-metal complexes which contain C, N, O, or S donor groups. Examples of these highly-conducting compounds are $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ ¹ (C donor), $[Ni(\text{phthalocyanine})](I_3)_{0.33}$ ² (N donor), $K_{1.81}[Pt(C_2O_4)_2] \cdot 2H_2O$ ³ (O donor), and $NH_4[Ni(\text{mnt})_2] \cdot xH_2O$ ⁴ (S donor). Of these compounds, only $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ and $[Ni(\text{phthalocyanine})](I_3)_{0.33}$ exhibit metal-like electrical conductivity ($\partial\sigma/\partial T < 0$). Although several organic donor-acceptor complexes which contain sulfur (TTF-TCNQ is an example)⁵ possess metal-like conductivity near room temperature, no transition-metal complex with an organic sulfur ligand has previously been reported to possess metal-like conductivity.⁶

As part of our overall effort to synthesize new, highly-conducting transition-metal complexes we have recently prepared samples of $K_2[Ni(DTO)_2]I_{1.0}$ (DTO = S, S' - 1,2-dithiooxalate dianion) which show metal-like conductivity in the temperature range 20-400 K. These samples were prepared by reacting three-times recrystallized $K_2[Ni(DTO)_2]$ ⁷ with a two-fold excess of I_2 in an evacuated, sealed glass tube for five days at 130-140°C. After this time the unreacted I_2 was removed under vacuum at 90°C. The copper-colored compound prepared in this manner reacts slowly with water if stored in air below 90°C. Chemical analysis⁸ of freshly-prepared samples were consistent with the formula $K_2[Ni(DTO)_2]I_{1.0 \pm 0.05}$. Although we have reproduced this preparation several times, these reaction conditions do not always produce a product with metallic conductivity. In fact, our success rate with this process has been three metal-like products in 24 attempted syntheses under (apparently) identical conditions. We have been unable to explain this marked irreproducibility. In the preparations which did not yield a product with metallic conductivity, I_2 uptake by $K_2[Ni(DTO)_2]$ occurs only

to the extent of 0.25 - 0.65 I per Ni. These "I deficient" products have room temperature electrical conductivities near $1 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$.

The electrical conductivity of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ is significantly higher than that which has been reported for other stacked transition-metal complexes, with compaction conductivities at room temperature on the order of $500 \Omega^{-1} \text{ cm}^{-1}$.

Figure 1 illustrates the temperature-dependence of the electrical conductivity of several samples of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$. These data were obtained by using pressure contacts on pressed pellet specimens. The four contacts were arranged in the van der Pauw configuration⁹ and supported in a specially-constructed low-temperature cell made of Teflon. Dc electrical conductivities were calculated from the following expression $\sigma(\Omega^{-1} \text{ cm}^{-1}) = 0.2206 \frac{I}{tV}$

in which I is the applied current, V is the observed voltage drop across the sample, and t is the sample thickness in cm. All the metallic samples of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ displayed ohmic behavior under the experimental conditions ($I = 10\text{--}90 \text{ mA}$). Data set A in Figure 1 was obtained with a freshly-prepared sample of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ powder which had been kept at 90°C prior to making the measurements. The conductivity of this sample increased slowly in the temperature range 373 to 250 K then increased more rapidly to 24 K. No metal-to-insulator transition was observed for this sample at $T \geq 24 \text{ K}$. In contrast, the conductivity of sample B (Figure 1) maximizes near 190 K. Sample B was stored at room temperature in air for several days prior to making the measurements. Below 190 K the conductivity of sample B dropped rapidly to approximately $1\Omega^{-1} \text{ cm}^{-1}$ at 80 K. A low-temperature maximum in the conductivity vs. T curve was also observed for sample C (Figure 1). This sample was a compaction of small ($\leq 100\mu$), copper-colored crystals of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}_{1.0}$. These crystals were obtained at a platinum anode by electrolysis (1.5 V) of a concentrated methanolic solution of $\text{K}_2[\text{Ni}(\text{DTO})_2]$ and tetraethylammonium iodide. This sample showed metal-like conductivity in the temperature range 300 to 90 K. At 90 K the conductivity of the sample began to decrease, reaching a value of $40 \Omega^{-1} \text{ cm}^{-1}$ at 22 K. We have as yet been unable to prepare single crystals of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ which are

large enough for single-crystal X-ray diffraction or for measurements of the anisotropy of conductivity.

Samples of $K_2[Ni(DTO)_2]I$ with metal-like conductivity are paramagnetic, as compared to highly-purified $K_2[Ni(DTO)_2]$ which is diamagnetic. The variable-temperature magnetic susceptibility and effective magnetic moment per Ni of highly-conducting sample A are shown in Figure 2. The value of μ_{eff}/Ni decreases from $2.6\mu_B$ at room temperature to approximately $2.2\mu_B$ at 40 K. Below 40 K the magnetic moment increases and becomes field dependent. This low-temperature behavior indicates the onset of ferromagnetic order in the material. In contrast to sample A, samples B and C behave as normal paramagnets over this entire temperature range ($\mu_{eff} \approx 2.4\mu_B$ at 300 K and $2.1\mu_B$ at 25 K.) We observe no magnetic anomaly for samples B and C in the vicinity of their metal-to-insulation transition temperatures (190 and 90 K, respectively.)

Although detailed analysis of the properties of $K_2[Ni(DTO)_2]I_{1.0}$ must await a single-crystal structural determination, our present conception of the bonding in this molecular metal involves localized magnetic states (molecular orbitals) of comparable energy to a partially-filled band formed by direct overlap of either d_{z^2} or ligand π orbitals on adjacent stacked $Ni(DTO)_2$ units. It is interesting to speculate that the metallic electrical conductivity of $K_2[Ni(DTO)_2]I_{1.0}$ may arise through formation of a band which is a strong admixture of both ligand and metal orbitals and that this strong intrachain bonding gives rise to enhanced stability of the metallic state in this compound.

Acknowledgement: This work was supported in part by the Office of Naval Research.

References and Notes

- (1) Krogmann, K.; Hausen, H.D. Z. Anorg. Allg. Chem. 1968, 358, 67.
- (2) Schramm, C.J.; Stojakovic, D.R.; Hoffman, B.M.; Marks, T.J. Science 1978, 200, 47.
- (3) Kobayashi, A.; Sasaki, Y.; Shirotani, I.; Kobayashi, H. Sol. State Commun. 1978, 26, 653.
- (4) mnt is the 1,2-dicyanoethylenedithiolate dianion: Perez-Albuerne, E.A.; Isett, L.C.; Haller, R.K. J. Chem. Soc. Chem. Commun. 1977, 417 and Miller, J.S.; Epstein, A.J. J. Coord. Chem. 1979, 8, 191.
- (5) Kistenmacher, T.J.; Phillips, T.J.; Cowan, D.O. Acta Cryst. 1974, B30, 763.
- (6) "Ionic" mixed-valence metal sulfides such as KCu_4S_3 are, however, known to possess high, metal-like, electrical conductivity ($\sigma^{4.2\text{K}} \approx 6 \times 10^5 \Omega^{-1}\text{cm}^{-1}$): Brown, D.B.; Zubieta, J.A.; Valla, P.A.; Wroblewski, J.T.; Watt, T.; Hatfield, W.E.; Day, P. in preparation.
- (7) Prepared from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and K_2DTCO (Eastman): Cox, E.G.; Wardlaw, W.; Webster, K.C. J. Chem. Soc. 1935, 1475.
- (8) C, H, and I analyses by Integral Microanalytical Laboratories, Raleigh, N.C.
- (9) Van der Pauw, L.J. Phillips Res. Rpts. 1958, 13, 1.

James T. Wroblewski and David B. Brown*

Department of Chemistry

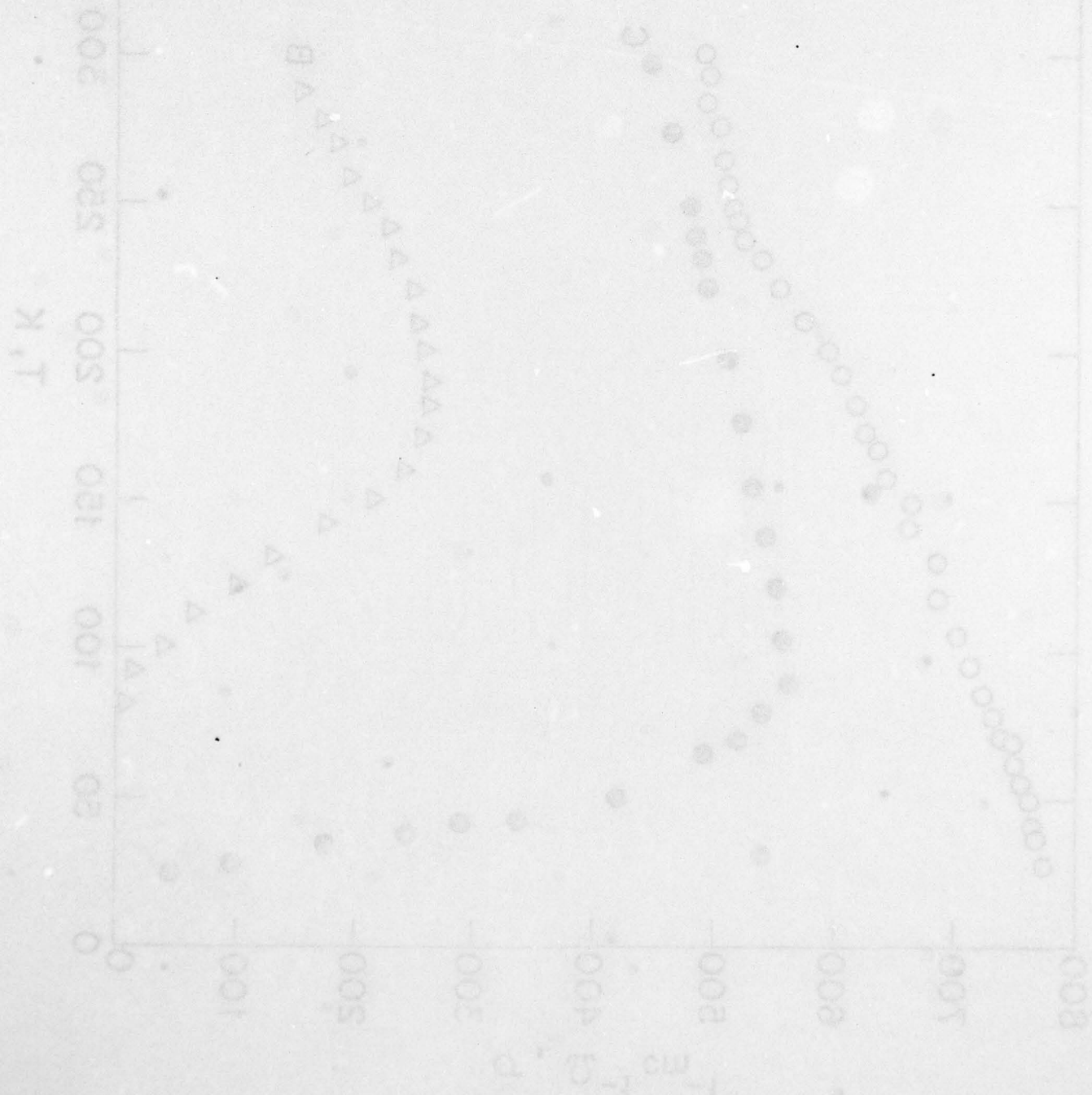
University of Vermont

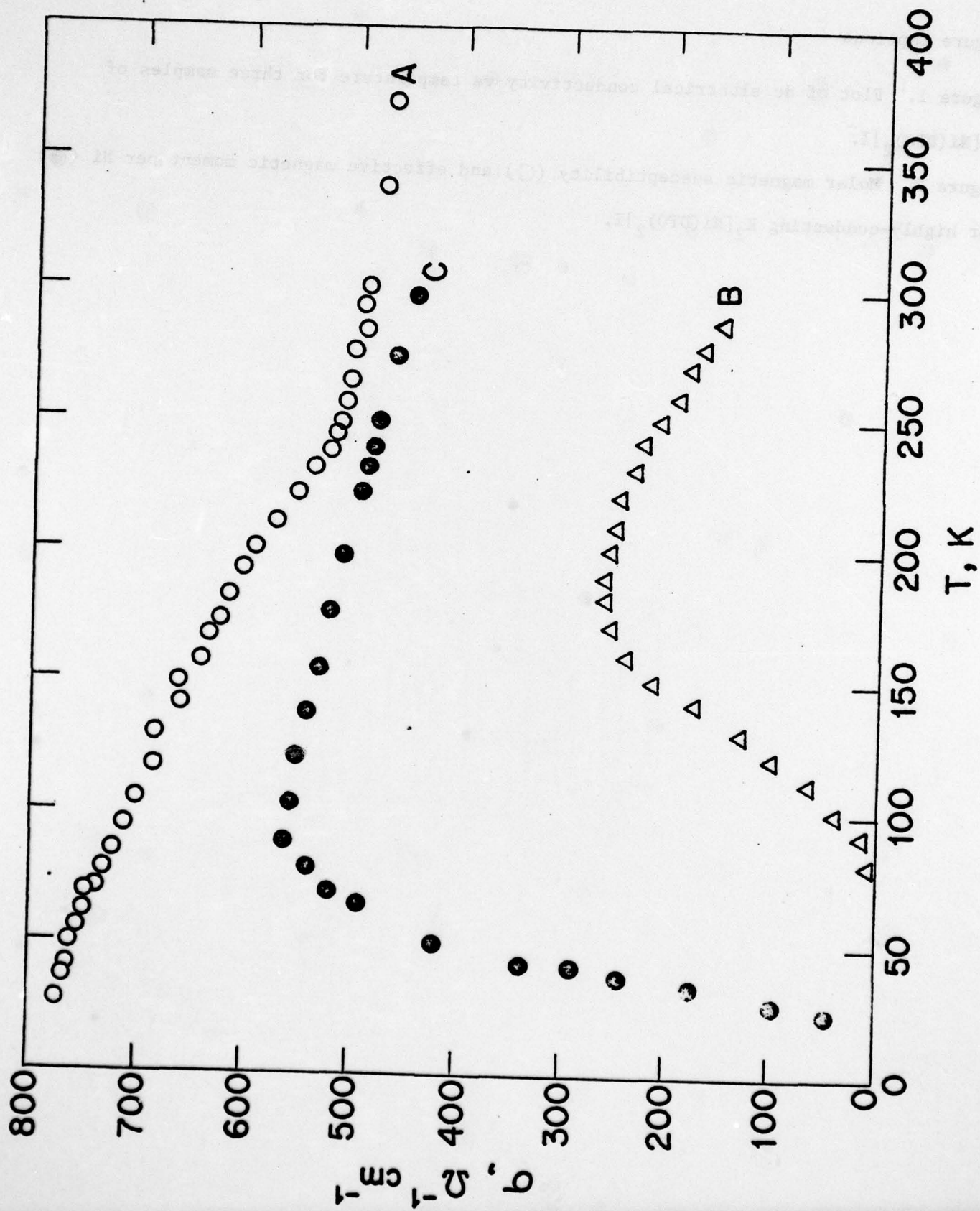
Burlington, Vt 05405

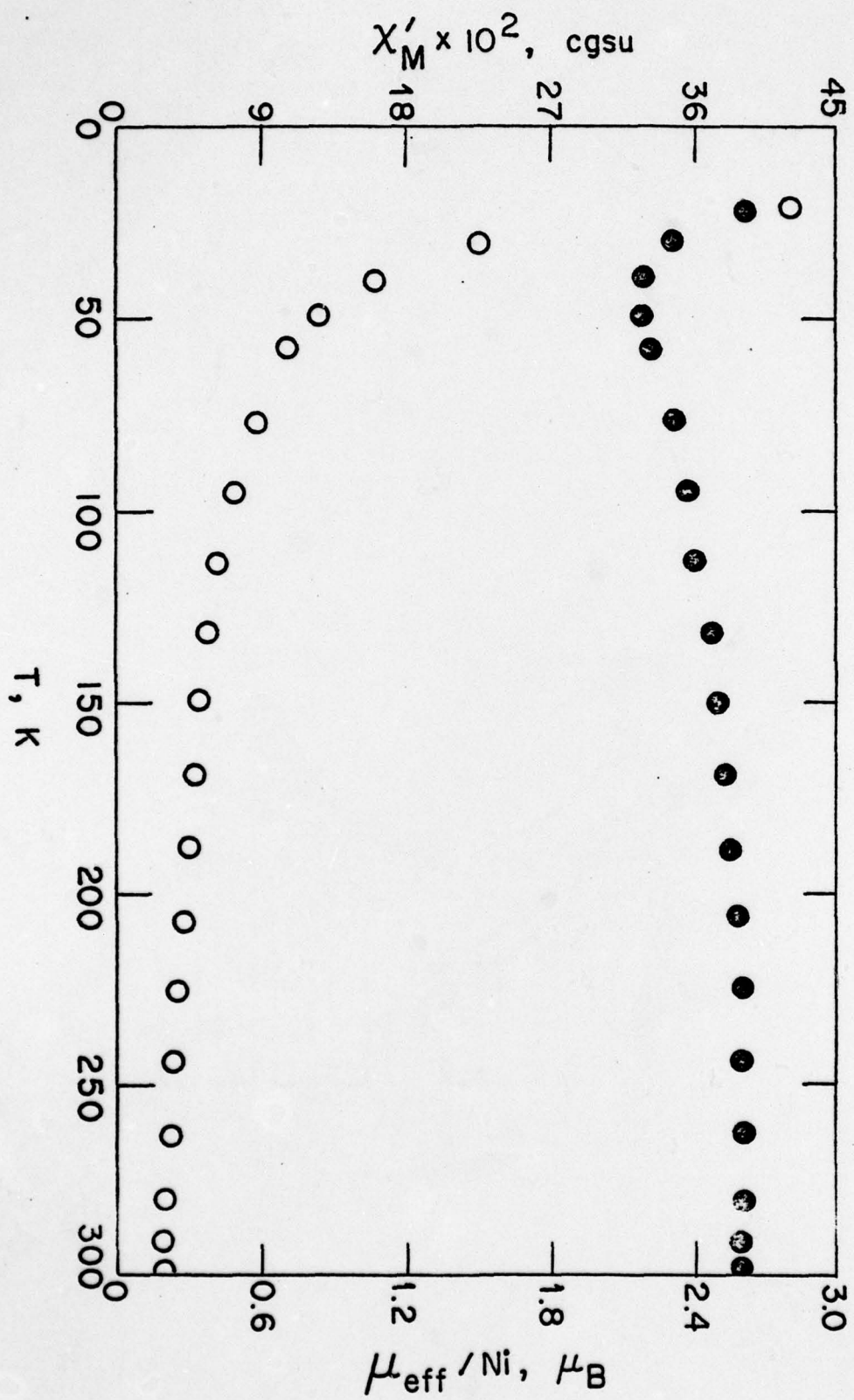
Figure Captions

Figure 1. Plot of dc electrical conductivity vs temperature for three samples of $K_2[Ni(DTO)_2]I$.

Figure 2. Molar magnetic susceptibility ($\bigcirc$) and effective magnetic moment per Ni ($\bullet$) for highly-conducting $K_2[Ni(DTO)_2]I$.







TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	U. S. Army Research Office P. O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
ONR Area Office One Hallidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Professor K. E. Woehler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Washington, D. C. 20390 Attn: Code 6100	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D. C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D. C. 20350	1	Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Commander, Naval Air Systems Command Department of the Navy Washington, D. C. 20360 Attn: Code 310C (H. Rosenwasser)	1	Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division	1
		Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	1

TECHNICAL REPORT DISTRIBUTION LIST, 053

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. R. N. Grimes University of Virginia Department of Chemistry Charlottesville, Virginia 22901	1	Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. M. Tsutsui Texas A&M University Department of Chemistry College Station, Texas 77843	1	Dr. B. Foxman Brandeis University Department of Chemistry Waltham, Massachusetts 02154	1
Dr. M. F. Hawthorne University of California Department of Chemistry Los Angeles, California 90024	1	Dr. T. Marks Northwestern University Department of Chemistry Evanston, Illinois 60201	1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D. C. 20375	1	Dr. G. Geoffrey Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. J. Adcock University of Tennessee Department of Chemistry Knoxville, Tennessee 37916	1	Dr. J. Zuckerman University of Oklahoma Department of Chemistry Norman, Oklahoma 73019	1
Dr. A. Cowley University of Texas Department of Chemistry Austin, Texas 78712	1	Professor O. T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214	1
Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1	Professor P. S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1	Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167	1